The Institute of Paper Science and Technology

Atlanta, Georgia

Doctoral Dissertation Reprint

AN INVESTIGATION OF THE MECHANISM OF ALKALINE SIZING WITH ALKENYL SUCCINIC ANHYDRIDE

A thesis submitted by

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from Lawrence University
Appleton, Wisconsin

June, 1987

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ABSTRACT

Sizing agents are used in paper and board products to retard the rate of penetration of liquids into the products.

One class of sizing agents is alkaline sizes. These materials are reputed to react covalently with cellulose. The covalent reaction is reported to be the method of both anchoring and orienting the alkaline sizes.

Several authors have questioned the existence or necessity of a covalent mechanism for the alkyl ketene dimer (AKD) alkaline size to promote sizing. Little direct chemical proof of a covalent bond has been offered in this system.

Similarly to AKD, the alkenyl succinic anhydride (ASA) sizes have always been reported to react covalently, and no direct proof of a covalent mechanism in the ASA system has been published.

The first phase of this thesis included the reaction of ASA and extracted cotton linters in N,N-dimethylformamide. A peak indicative of an ester was found using diffuse reflectance infrared Fourier Transform spectrometry (DRIFTS) at about 1732 cm^{-1}. Also included in this phase was the determination by DRIFTS that an ester of ASA was formed under papermaking conditions. A cotton linters handsheet containing ASA and a cationic retention aid, poly(1,2-dimethyl-5-vinylpyridinium bromide) (DMVPB), was the system used for examination.

In the second phase of this thesis, conditioning time, drying time and drying temperature were varied, and ASA sizing and reaction were related to these variables. Increased drying temperatures improved sizing and increased the reaction rate. Increased drying times benefited sizing and increased the reaction to a point. Sizing fell with long drying times. Conditioning yielded increased sizing and reaction at low drying times, where ASA could be expected to remain after drying.

In the final phase of this thesis ASA was found to migrate during drying, but not during conditioning, to yield sizing through esterification. Esterification of ASA continued during conditioning. Sizing also increased during conditioning and was related to curing of the ASA.

INTRODUCTION

A sheet of paper or paperboard is made up primarily of cellulose. One of the latter's most important properties is its ability to adsorb and absorb water. This property allows the sheet to be formed, dispersed as broke, and to act as an absorbent product. While this property may be desirable under certain conditions, under other conditions the ability to readily affiliate with water is not desirable in a product.

Products such as writing paper, bag paper, and food wrap must resist liquid penetration to maintain the fiber bonding that provides them their useful structure. There are two ways to maintain structural integrity in paper exposed to liquids. The first of these is to use a wet-strength agent. These materials are thought to protect the interfiber bonds in some way.[1] The second method is to use sizing agents. These materials yield liquid resistance by virtue of their nonpolar natures. While having in most cases a polar region as well as a nonpolar region, it is their nonpolar portion that when properly oriented serves as a barrier to polar, aqueous penetrants. This latter method of liquid protection is the subject of this thesis.

CHEMICAL BONDING

There are many types of bonds that may be formed between two materials (intermolecular) and within a single material (intramolecular).

The three strongest types of recognized bonds are (1) ionic, (2) metallic, and (3) covalent. The third type of bond, covalent, is the only one of the above three bonds of interest here. This type of bond involves the sharing of a pair of electrons with opposite spins. It is possible to have more than one covalent bond between atoms, such as in the case of nitrogen (N_2).[2]

There are also weaker intermolecular and intramolecular forces. One of these forces is termed hydrogen bonding.

Hydrogen bonding, as noted above, may be intermolecular or intramolecular. This form of bond involves the interaction of a proton donor group with a site of high electron density. The proton donor group is of the form AH, where A may commonly be nitrogen or oxygen. The site of high electron density may be a lone pair of electrons, or the pi electrons of a multiple bond.[3]

INTERNAL SIZING

Certain papers and boards must be sized because cellulose is a hydrophilic material, having a relatively high surface energy. Sizing agents retard liquid penetration by providing a surface of lower energy. This allows these sized cellulosic products to function as desired even in the presence of liquids.

A sheet of paper may be thought of as a network of pores. The rate of penetration of a liquid into a pore may be roughly described by the Washburn equation as shown in Eq. (1).[4] Since the pore radius, pore depth, surface tension and liquid viscosity are difficult to control, the easiest approach to controlling liquid penetration is to alter the contact angle.

$$\frac{dl}{dt} = \frac{\gamma r}{4\eta l} \cos\ominus \qquad (1)$$

where: r = pore radius

γ = surface tension

η = viscosity

l = pore length

θ = contact angle

t = time

Sizing agents increase the contact angle and must produce a contact angle greater than 90 degrees to retard liquid penetration. The contact angle is shown in Fig. 1.

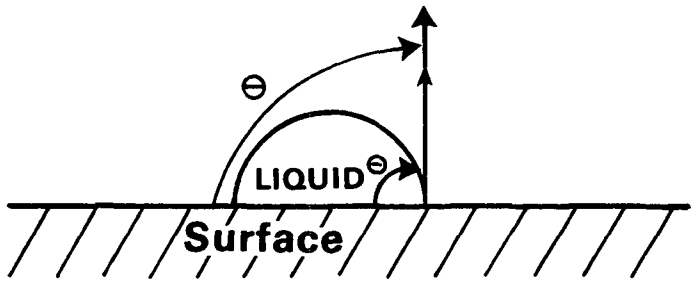


Figure 1. Contact angle of 90°.

To accomplish the above requirement, a hydrophobic tail must be oriented such that a barrier is presented to the penetrant. This provides a surface of low energy. Orientation of the size molecule is therefore very important.

Additionally, the size molecule must be well anchored on the fiber surface and be relatively inert to the material it must size against, so that a reaction can not disrupt the mechanism by which the sizing agent retards penetration. The size molecules must also be well distributed on the fiber surface.

When the above conditions are met, very little sizing agent is required to effectively protect the fiber against penetration.[5-7] Davison[4] places the amount at 0.0005 gram of size per square meter of fiber surface.

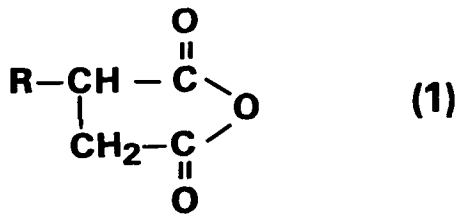
The Rosin-Alum System

The most well-known sizing system utilizes rosin, a mixture of resin acids. These acids contain a large nonpolar group and a single polar carboxylic acid group in each molecule. Also used in this system is papermakers' alum, hydrated aluminum sulfate.[8]

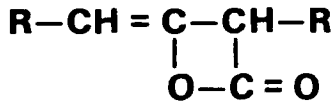
Alum, as a cationic species, is used to anchor the rosin to cellulose ionically, and to orient the nonpolar group of the rosin such that the group presents a hydrophobic barrier to penetrants.[6] Since the aluminum species varies with pH, and successful sizing is dependent on providing the appropriate aluminum species, the pH range of this system is acidic, usually being restricted to 4.0-5.0.[4,9]

Alkaline Sizing

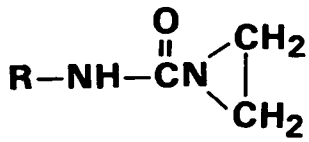
Alkaline sizes may be defined as sizes that have the ability to function over a broad pH range, especially when compared to the traditional rosin-alum system. Alkaline sizes are also commonly considered to include sizes with a cellulose-reactive end group, such as are shown in Fig. 2.[10]



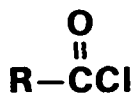
(1)



(2)



(3)



(4)

where: R = carbon – hydrogen tails

Figure 2. Sizing agents with reactive end groups.

Reasons For Use

Alkaline papermaking is presently used to produce about 10-15% of the fine papers made in the United States. In Europe, alkaline papermaking accounts for about 50% of the fine paper production.[11]

The reasons for using the alkaline sizes are numerous and have been detailed by several authors.

Among the reasons noted are (1) the ability of the alkaline sizes to size against water and nonaqueous liquids, (2) the ability to use calcium carbonate, a high brightness filler, which is not possible in the pH range in which rosin-alum systems must operate, (3) the ability to produce a sheet that will not weaken and embrittle with time, which is not possible in an acidic system, (4) the ability to produce a stronger sheet in the pH range that alkaline sizes are used than in that of the effective alum pH range, (5) reduced corrosion in the alkaline, as compared to the acidic, system, (6) increased closure of the water system, since the ionic environment in an alkaline system is less concentrated than that of a rosin-alum system, (7) high levels of filler are possible as a result of the increased sheet strength, (8) lower energy requirements, (a) in sheets containing high amounts of filler because drying filler is easier than drying fiber, and (b) because less refining for strength properties is required, and (9) overall economic benefits resulting from the preceding advantages.[10,12,13]

Common Alkaline Sizes

The sizes used in alkaline systems are primarily of three types. These are (1) alkyl ketene dimers (AKD), (2) linear stearic anhydrides, and (3) alkenyl succinic anhydrides (ASA). General characteristics of alkaline sizes are reactive end groups and long, hydrophobic tails.

ASA and AKD are the alkaline sizes used most often and are shown in Fig. 2 as compound (1) and compound (2), respectively. Each size has advantages and disadvantages when compared with the other.[10]

AKD sizes have a four-membered lactone for a functional end group, while ASA sizes are five-membered cyclic anhydrides. Both of these sizes are used in the liquid form and are insoluble in water, so they must be emulsified for use in a papermaking system. The rate of curing of ASA is greater than that of AKD. AKD may cure so slowly that surface sizing, which is dependent on internal (i.e., wet end addition) sizing to limit penetration, may be difficult to control.[10]

Preparation and Theoretical Mechanism

In contrast to the more commonly used rosin-alum system, alkaline sizes, as noted above, are added as emulsions to/the stock system. Various dispersants and stabilizers may be used for emulsification.[10]

The emulsified size droplets must be retained on the fiber in order to obtain sizing. This may be done using cationic agents such as alum, polymers, and modified starches.[14] Additionally, cationic emulsifying agents may be used.

The cellulose on which the size must be deposited is negatively charged. The charge on a solid surface is thought to develop as a result of (1) ionization of molecules, or (2) adsorption of ions from the surrounding solution onto the surface of the solid.[15] Retention of the size particle is the result of ionic attraction of the cationic emulsion droplets to the negatively charged cellulosic fiber.

Once the size has been retained on the fiber, the functional end group of the size reportedly reacts with the cellulosic hydroxyl groups to form covalent bonds. This reaction is shown for ASA and AKD in Fig. 3. In the case of AKD, a β-ketoester would be formed. The reaction of ASA would yield an ester-acid, though the carboxylic acid could be replaced by the carboxylate anion, depending on the alkalinity of the system. Necessary to these reactions is the addition of heat, for example, from the paper machine's dryer system.[10,13,16,17]

In addition to the reported covalent reaction with cellulose, the sizes may also undergo hydrolysis, yielding carboxylic acids. AKD may react further, through decarboxylation, to yield a ketone. This reaction is shown for ASA and AKD in Fig. 4. The acids could be formed as carboxylate anions depending on the system's alkalinity. These hydrolysis products are generally considered undesirable in the stock system and are thought to be inefficient as sizing agents.

The reactivity of the different sizes, as it affects the covalent bond formation with cellulose, will also affect the hydrolysis reaction. Thus, while AKD sizes react slowly with cellulose relative to ASA sizes, they also hydrolyze more slowly, and are more stable in the emulsified form. The chemistry of alkaline sizing is therefore dependent on achieving a balance between the two competing reactions.[10,12]

Other Chemicals and Considerations

Other system factors are important to the effectiveness of the alkaline sizing agents. In the case of AKD a pH above 7.5 is preferred in the stock system. This is especially true if alum is used in the system with the size, since alum may be harmful to AKD sizing.[6,17-19]

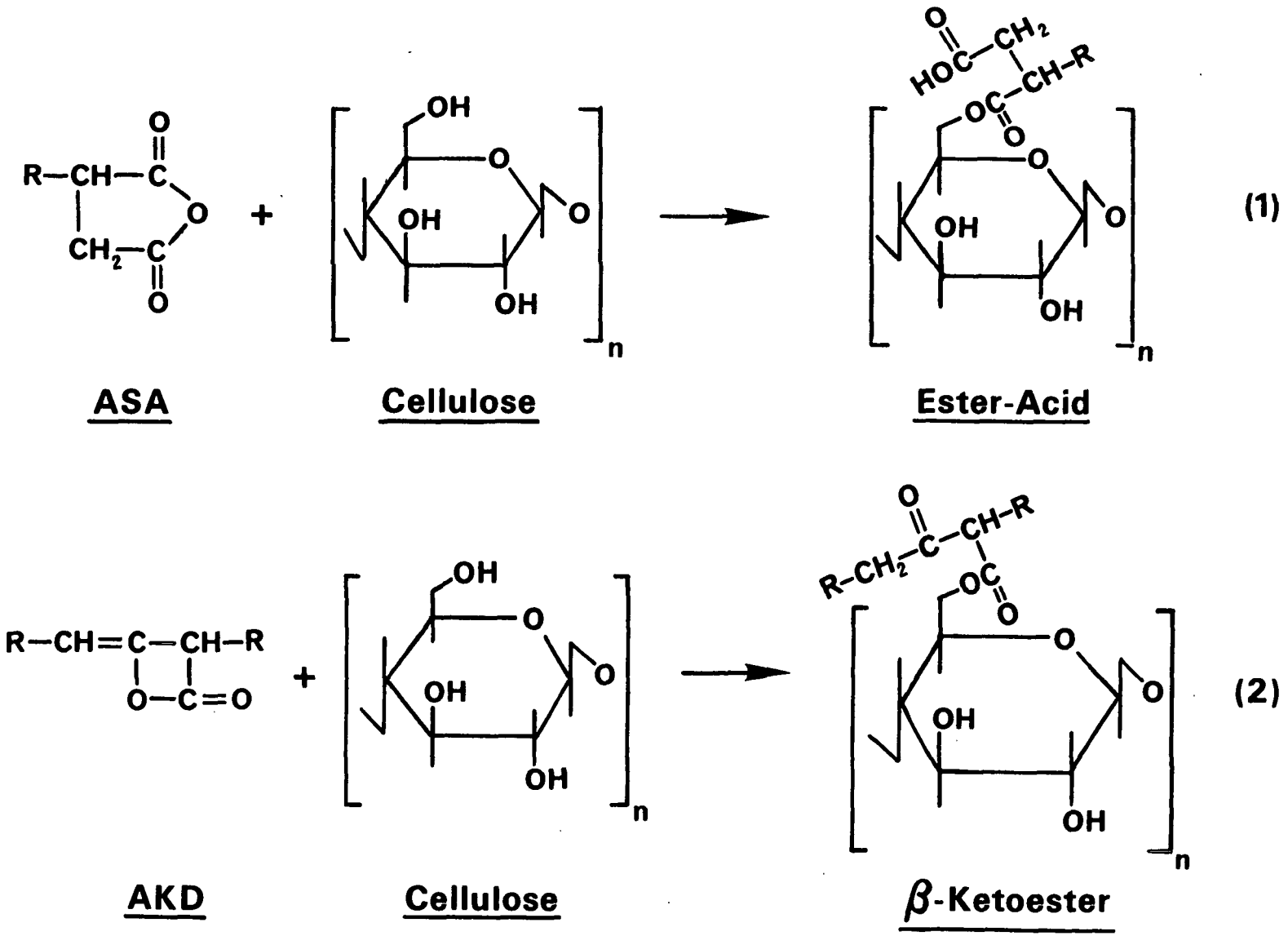


Figure 3. Reactions of ASA and AKD with cellulose.

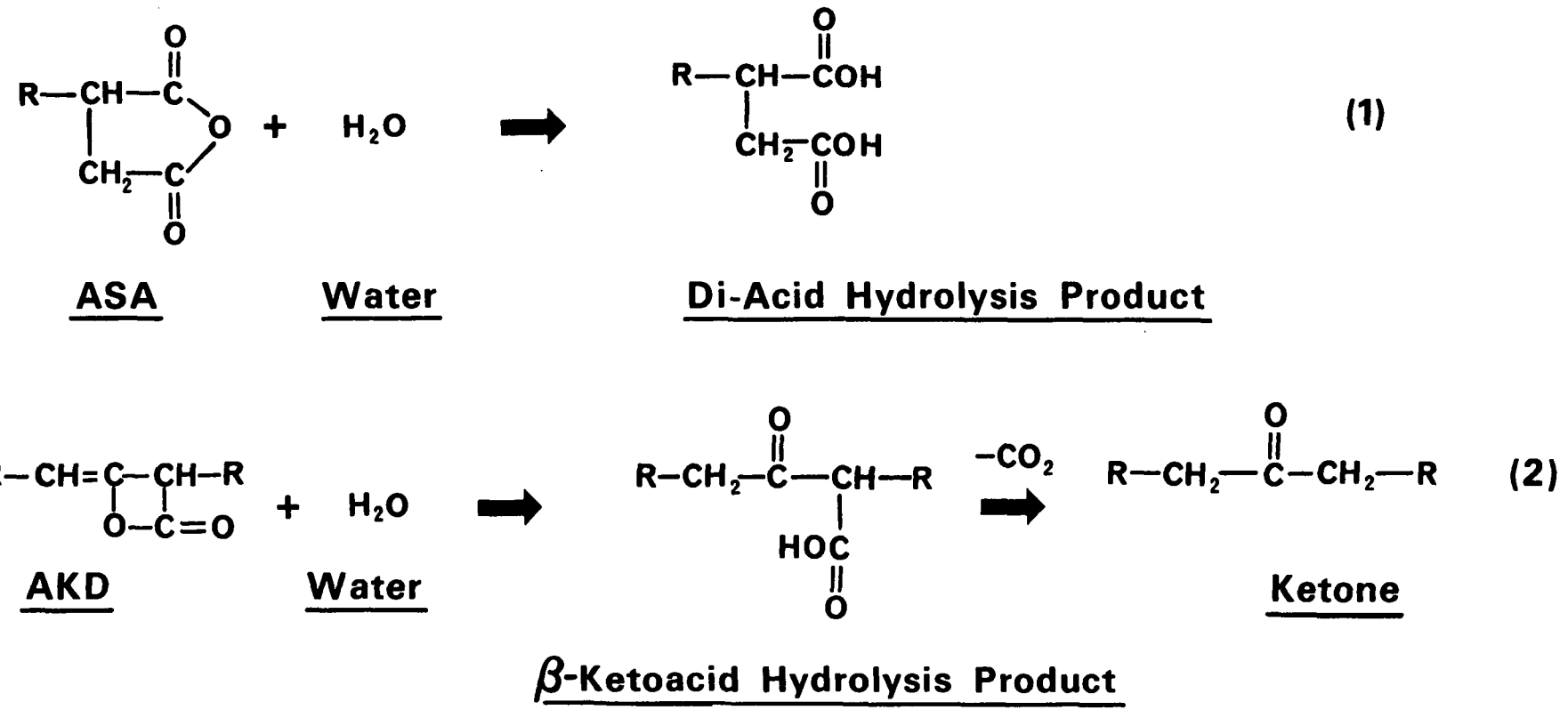


Figure 4. Reactions of ASA and AKD with water.

In the case of ASA sizes the reported pH range of operation is broader, from 4.5-8.0. The suggested pH range is 7.0-8.0. Additionally, alum appears to benefit the ASA system up to a certain level.[6,20]

ANHYDRIDE CHEMISTRY

Anhydrides are composed of two carbonyl groups linked by an oxygen atom and may be of two distinct forms, (1) linear and (2) cyclic, as shown in Fig. 5.

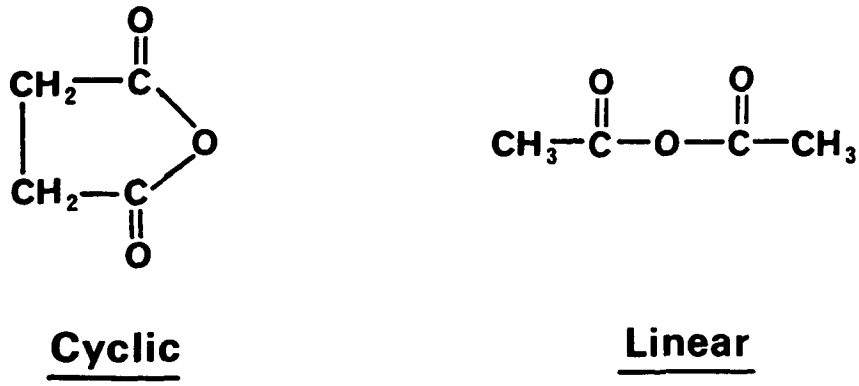


Figure 5. Types of anhydrides.

Anhydrides are less reactive than acid chlorides, but are more reactive than esters, carboxylic acids, or other carboxylic acid derivatives. Anhydrides will react by nucleophilic acyl substitution with water, alcohols, ammonia, and amines to form carboxylic acids, esters, and primary and secondary amides, respectively. These reactions are shown in Fig. 6. The presence of mineral acid or hydroxide ions will significantly increase the hydrolysis reaction. Similarly, mineral acid or alkoxide ions will increase the rate of the alcoholysis reaction.

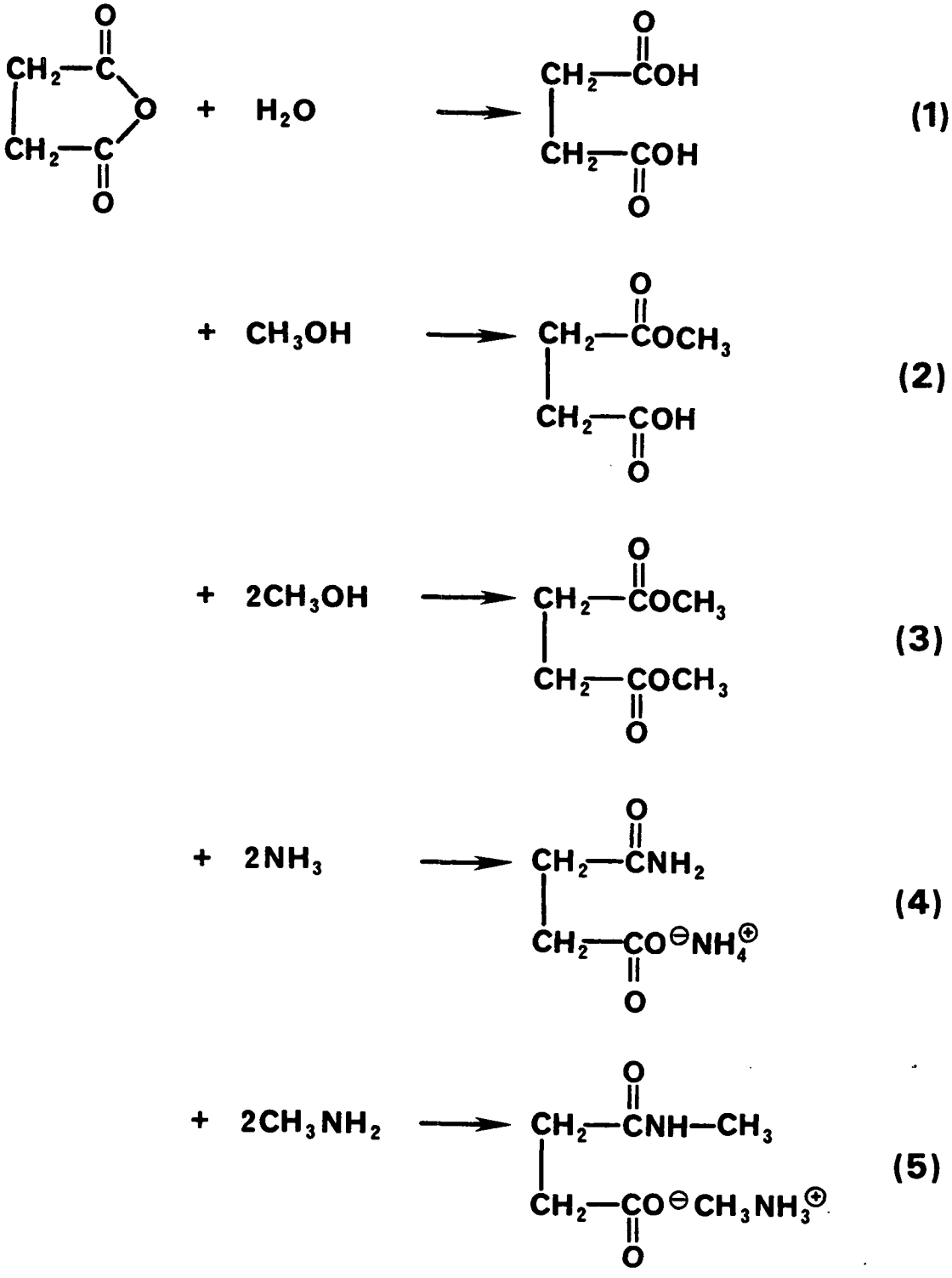


Figure 6. Reactions of anhydrides.

In cyclic anhydrides it is possible to form either a diester or an ester-acid during alcoholysis, depending on the amount of alcohol present. These two possibilities are shown in Fig. 6.[21,22]

AKD: LITERATURE REVIEW OF THE REACTION WITH CELLULOSE AND THE MECHANISM

Since AKD and ASA are reported to react with cellulose in a similar manner, and because results reported by some of the sources cited below stimulated this thesis, a review of pertinent AKD literature is provided here.

Davis, Roberson, and Weisgerber[16] provided evidence for covalent reaction of AKD with cellulose. They stated that AKD cannot be solvent extracted after reaction, and that sizing is unaffected by extraction. Additionally, they observed that following reaction with AKD, the fiber is no longer completely soluble in a cuprammonium solution. A fiber shell, indicative of surface reaction, remains. In contrast, fiber that is not treated with AKD is completely soluble.

Enke[23] used a bleached spruce sulfite pulp and two types of AKD with cationic starch. Sheets were treated with melted AKD, or AKD in carbon tetrachloride. By a combination of extraction and infrared (IR) spectrometry work, it was determined that approximately 85% of the AKD on the fiber reacted in a chemical manner with cellulose. The remaining 15% of the AKD on the fiber was physically adsorbed. The IR methods used included conventional spectrometry of a carbon tetrachloride extract and multiple internal reflectance (MIR), or attenuated total reflectance (ATR) spectrometry of a test sheet.

Pisa and Murckova[24] identified the bond between AKD and cellulose as a hydrogen bond involving the oxygen atoms of the lactone ring and the hydroxyl

groups on cellulose. It was suggested that prior to the formation of the hydrogen bonds the size was retained on the fiber as a result of a cationic starch retention aid and was subsequently distributed over the fiber because of melting during the drying phase. Only on completion of the distribution did the hydrogen bonds form. It was suggested that the hydrogen bonds formed result in an orientation of the AKD molecule such that the lactone ring faces the fiber, while the hydrophobic tail is oriented such that it can repel approaching liquids.

Pisa and Murckova also used MIR IR spectrometry methods in their studies. In addition to examining the spectra of sheets, they also examined model systems of the AKD and alcohols (methanol, 2-propanol, and ethylene glycol). The purpose of the model systems was to determine whether β-ketoesters (the reported AKD-cellulose reaction product) could be formed. In model systems IR absorption spectra did show formation of the β-ketoester.

In addition to the model systems, Pisa and Murckova also examined IR spectra of the starch emulsified size. They noted that there was some evidence of the formation of a β-ketoester between the starch and the AKD. They also noted that the formation of hydrogen bonds between the starch and AKD was suggested by the shifting of band frequencies.

In examining sheets of sized paper, no evidence of the formation of a β-ketoester was found. Again, it was found that there was evidence of AKD hydrogen bonding, as there was a band shift when the spectra of the sized sheets were examined. Also of interest was the fact that it was claimed the orientation of the AKD molecule on the cellulose, due to hydrogen bond formation, could be followed by IR monitoring of two bands. As the AKD became oriented the ratio of the intensities of the two bands changed (decreased).

Kamutzki and Krause[25] used a high performance liquid chromatograph (HPLC) and a variety of solvents in their study of the AKD sizing system. It was claimed that a chemical reaction between AKD and cellulose occurred during drying. Additionally, methods for quantitatively extracting the size and its reaction products from both the white water and sheets were suggested. It should be noted that Kamutzki and Krause specified that the extraction of the reacted AKD from sheets still required more investigation and improvement.

While it was suggested that a chemical reaction between the AKD and cellulose occurred, there was apparently no effort made to identify the reaction product. On deciding that a reaction had occurred, they concluded that the ester of the AKD had been formed with cellulose.

In more detail, Kamutzki's and Krause's investigation involved six steps: (1) HPLC separation of the size, followed by mass spectrometric (MS) identification of the fractions, (2) extraction of residual AKD and its reaction products from white water by freeze-drying the samples, (3) extraction of the sheet to remove AKD and its reaction products, (4) determination of the retained AKD by extraction of sheets after pressing and an investigation of the effects of various parameters on AKD retention, (5) extraction and identification of the extractable materials in the sheet (a) as drying progresses and (b) with increasing time after drying, and (6) addition of dilute caustic to the sheet, followed by extraction of the sheet, to remove the supposedly cellulose reacted AKD.

Using this procedure Kamutzki and Krause suggested (1) in wet end operations the size is retained and partially hydrolyzed, (2) during drying the

ester bond between AKD and cellulose is formed, and hydrolysis still occurs, and (3) after drying the esters are still being formed, and hydrolysis still continues.

Kamutzki and Krause[26] used AKD sized Rapid-Kothen (RK) sheets and a HPLC system to examine reaction products extracted from sheets. It was found that machine-made papers had up to 30% of the AKD converted, through hydrolysis, to ketones. In contrast, RK sheets contained only 3-5% of the ketones. They suggested that the ketone formation was influenced by the formation method and by drying factors. Additionally, it was found that both machine-made and RK sheets contained unreacted AKD.

In investigating RK sheet drying effects, it was determined that high drying temperatures in sheets are obtained only after most of the water is removed. It was suggested that this was the reason few ketones were formed. Additionally, it was shown that higher preliminary drying temperatures lead to improved sizing.

Investigation of pH effects led to the conclusion that sizing was optimum under neutral or alkaline conditions. The pH findings were explained by the following:

> "although protonization of the C=O group on the lactone ring in the acid range leads to higher electrophilia on the reacting carbon, which means that the sizing reaction in the acid range is only slow, even in the presence of many protons, this protonization is crucial. Reaction with the cellulose is, on the contrary, accelerated by the strengthening of the nucleophilia of the hydroxyl groups of the cellulose as a result of the increased number of hydroxyl ions in the neutral and alkaline range, respectively."

Kamutzki and Krause also suggested that large increases in sizing are achieved by increasing the reacted AKD only a few percent.

Gupta[27] pretreated fiber with AKD and found that when a sheet contained 5% of the pretreated fiber, the sizing performance was equivalent to conventional wet end AKD sizing. Additionally, losses of the size to the white water were avoided.

Rohringer, Bernheim, and Werthemann[28] used AKD to study the alkaline sizing reaction mechanism. In discussing Gupta's[27] work, Rohringer, Bernheim, and Werthemann[28] suggested that a likely explanation for those results would be migration of the AKD through the sheet. This would eliminate the possibility of a covalent AKD-cellulose bond. They also suggested and performed tests to determine whether a covalent bond was formed between AKD and cellulose.

To detect sizing migration, a multilayered sheet containing AKD on one side was tested for the level of sizing on both sides as time increased. It was found that sizing development of the unsized side of the sheet paralleled and approached the sizing development of the sized side.

To determine whether such apparent migration was possible with a size that is known to covalently bond to cellulose, stearoyl chloride was reacted with cellulose and the ester bond identified by MIR IR spectrometry. Using this modified fiber, mixed with unmodified fiber in levels up to 50%, no significant transfer of sizing as Gupta[27] found was determined. Rohringer, Bernheim, and Werthemann[28] knew that a 100% stearoyl chloride modified fiber sheet would be highly sized, and it was therefore concluded that a chemically bound size cannot migrate or provide sizing protection to unsized fiber even at 1:1 levels.

In attempting to identify the reputed β-ketoester bond between cellulose and AKD, MIR IR spectrometry was used; no β-ketoester bond was found.

In an additional experiment, AKD was mixed with α-methyl-D-glucopyranoside, and the melting points of the individual chemicals, and the mixture, were determined by differential scanning calorimetry. It was determined that no heat developed or was consumed, except that due to melting. Thus it was concluded no chemical bond could have been formed. Experimentation with AKD and starch yielded similar results.

In further experimentation, AKD was reacted to form the β-ketocarboxylic alkali metal salt. This chemical was able to provide sizing to the fiber. This suggested that AKD could react with other components of the papermaking system, besides cellulose to impart sizing to the fiber. Additionally, derivatives of AKD that could not react showed no sizing ability.

Miller[19] found, on heating stacks of AKD sized sheets on one side, that the sizing decreased near the heat source, and that there was a gradient across the stack with sizing showing less of a decrease as the distance from the heat source was increased. This would indicate that the sizing agent migrated away from the heat and that no covalent bond was involved.

Metzler[29] used MIR IR spectrometry techniques with AKD surface sized sheets. No evidence was found of an AKD-cellulose ester. Some evidence of weak hydrogen bonding with cellulose was provided at the lactone's carbonyl oxygen. As in Pisa's and Murckova's[24] work, Metzler[29] found some indication of a variation in the size's orientation with time.

Merz, Rohringer, and Bernheim[30] used C^{14}-labeled stearyl diketene (i.e., AKD) in combination with tetrahydrofuran and an HPLC to study alkaline sizing. They

determined that (1) up to 10% of the size cannot be extracted from the sheet after drying, (2) drying at elevated temperatures creates hydrolysis products, (3) room temperature drying is sufficient to develop sizing, and (4) reaction of the size with cellulose is not necessary to develop sizing. They noted that they could not exclude the possibility that there was some size reacted with cellulose in the unextractable portion.

Roberts and Garner[31] reacted water, propanol and methanol with diketene and AKD in organic solvents. The results were analyzed using IR methods and gas-liquid chromatography (GLC). Additional reactions were performed using methyl-β-D-cellobioside with diketene and AKD. These results were analyzed by proton nuclear magnetic resonance spectrometry (H-NMR). Both base catalyzed and non-catalyzed reactions were examined in all cases.

It was generally found that base catalyzed reactions with water and alcohols were much faster than noncatalyzed reactions, which were very slow, and that reactions, both catalyzed and noncatalyzed, with methyl-β-D-cellobioside were very limited, or nonexistent. It was concluded that formation of a covalent bond between AKD and cellulose would be very unlikely.

In another publication by Roberts and Garner[32], C^{14}-labeled AKD and hexadecyl hexadecanoate (HHD) were used to size handsheets. Heat treatment of the sheets resulted in much more efficient sizing for the AKD, than for the HHD. Additionally, at lower retention levels the AKD was much more effective than the HHD, and autoradiographs of AKD sized sheets showed that migration of the size occurred as a result of heat treatment.

Organic extraction of HHD and AKD sized sheets that had been heat treated showed that almost all of the HHD, which would not be expected to form an ester, could be removed and sizing returned to the unsized sheet's level, while 3-5% of the AKD remained in the sheets and sizing was not decreased. Extracted AKD was of an unreacted form.

Roberts and Garner concluded that there were thus three possibilities. The unextractable AKD is either present as an ester reacted with cellulose, present as an adsorbed monolayer that is difficult to extract, or present as a species polymerized during heat treatment.

Poppel and Bobu[33] examined the reactive properties of AKD. In general, they determined that an alkaline pH was beneficial to sizing. Further, they showed that higher drying temperatures yielded higher sizing levels, and that polyamide-polyamine-epichlorohydrin (PPE) resin also benefits sizing.

Variations in the drying time were also examined. Increasing the drying time caused sizing to increase. Additionally, when PPE was present the curing time was lower.

Though it is questionable whether AKD would have any significant charge, Poppel and Bobu suggested that PPE interacts ionically with AKD to decrease AKD hydrolysis. Additionally, they concluded that AKD could function as a sizing agent only if it were covalently reacted with either a polymer or cellulose, thereby being irreversibly bound to the fiber.

Nahm[34] reacted pulp, cellulose model compounds and microcrystalline cellulose in N,N-dimethylformamide with AKD. N-methylmorpholine was employed as a

catalyst. The model compounds used were methyl-α-D-glucopyranoside, cellobiose and maltose. The pulp used was a hardwood/softwood bleached kraft pulp.

In the case of the methyl-α-D-glucopyranoside reaction, evidence of the formation of a nonenolized β-ketoester was found by IR spectrometry and C^{13}-NMR examinations of the product. In the case of the other substrates, IR examination of the products also provided evidence of a nonenolized β-ketoester. Additionally, the results suggested a degree of substitution greater than one was possible.

Lindstrom[35] used a C^{14}-labeled AKD, cationic starch, a fines-free bleached softwood kraft pulp, tap water and a Finnish sheet former in his investigations. The sheets formed were extracted in tetrahydrofuran to remove unreacted AKD, dried, and burned to evolve the remaining AKD as C^{14}-labeled carbon dioxide. The carbon dioxide concentrations were determined by liquid scintillation and related to the amount of reacted AKD. Cobb sizing tests were also performed.

Lindstrom found that the AKD reaction rate was proportional to the pH and the drying temperature. The pH was found to have no effect on the reacted AKD required for sizing. In the work reported it was determined that a maximum of 50% of the AKD added could react with cellulose. Based on a $Cobb_{60}$ value of 25 g/m^2, Lindstrom reported that only 0.01% AKD (based on pulp) needed to react to provide sizing.

Lindstrom and Odberg[36] used MIR IR spectrometry techniques to examine AKD treated paper for ester peaks. The paper, made from a bleached softwood kraft pulp, was treated with AKD in tetrahydrofuran, air dried, and dried for 30

minutes at 110°C. The paper was then swelled in water and extracted in tetrahydrofuran. IR spectra of the paper were recorded after (1) impregnation, (2) curing, and (3) extraction.

It was found that the ratio of the lactone peak's intensity at 1850 cm^{-1} to the C-H stretching peak's intensity at 2916 cm^{-1} decreased after curing, and more so after extraction. This was explained as being due to AKD reaction and removal. Additionally, a small peak at 1745 cm^{-1}, indicative of the β-ketoester formed between cellulose and the AKD, was found. The peak was used to estimate an ester concentration of 0.047%.

In addition, Lindstrom and Odberg used calorimetry to examine the AKD reaction. Using pulp impregnated with (1) dichloromethane and (2) dichloromethane and 1% AKD, it was found that the second pulp had excess generated heat, indicating a reaction had taken place. The half-life of the reaction was estimated at 8.6 hours under the conditions used. At higher temperatures used in other work it was estimated a half-life of 5.2 hours was likely.

Lindstrom and Soderberg[37] used a C^{14}-labeled AKD and sheet combustion combined with extraction as described previously in other work.[35] Lindstrom and Soderberg[37] found that the $Cobb_{60}$ sizing level was directly related to the amount of AKD reacted with the fiber. Mechanical pulps were determined to require more reacted AKD than chemical pulps to obtain the equivalent sizing level. It was observed that the hydrodynamic wet specific surface area was not related to the sizing level, while the BET surface area was. It was also determined that most of the AKD reacts after the sheet is dry (> 90% solids), and that unreacted AKD provided sizing only in the presence of reacted AKD. The effectiveness of the reacted AKD was 2-3 times that of the unreacted AKD.

Lindstrom and Soderberg suggested that the AKD must spread before reacting, and that the AKD can spread only at an air interface occurring after the sheet is dry. AKD trapped between fibers was suggested to be unable to spread while trapped and, therefore, could yield no sizing through reaction. Further, it was suggested that AKD trapped between fibers can escape to spread and react, thereby providing sizing.

In other work, Lindstrom[38] was able to determine that small measurable quantities of the AKD could volatilize during drying. Lindstrom also concluded that pseudo-first order kinetics could describe the AKD reaction, and that activation energies of 54 and 72 kJ/mole at pH's of 10 and 4, respectively, were probable.

In freeze dried sheets it was determined that 10% more AKD could react than in normal sheets. Additionally, normally dried sheets containing AKD, when slushed and recured, also displayed an increase in reacted AKD. Further, it was concluded that the factor limiting the rate of AKD sizing is the chemical reaction, not AKD spreading.

In other work, Lindstrom and Soderberg[39] found that sodium bicarbonate increased the AKD reaction rate constant, and that sodium chloride and other salts slightly increased the reaction rate constant. Cationic basic amines were also determined to increase the AKD reaction rate constant. Sodium bicarbonate caused the amount of AKD reacted to increase, while the AKD retention was lowered.

PPE was determined to accelerate the AKD reaction rate, and when PPE is present an increase in pH will provide an increased AKD reaction rate constant. Further, it was observed that the combination of sodium bicarbonate and PPE resulted in an increase in the AKD reaction rate constant.

Dumas and Evans[40] used C^{14}-labeled AKD, sheet extraction, and sheet combustion to measure the retained and reacted AKD in handsheets. They observed that the amount of AKD reacted and retained varied with the pulp used. Further, they determined that the amount of reacted AKD could not be related to the sizing level when different pulps were compared. It was found that sizing increased as the retained and reacted AKD level was increased, and that conditioning resulted in increases in the sizing level.

In examining drying effects, Dumas and Evans observed that drum drying was more effective than air drying in yielding sizing. It was also shown, using laminated sheets, that excessive contact time with water at high temperatures detrimentally affects sizing.

Poppel and Bobu[41] utilized ultraviolet (UV) determinations of the AKD in white water to perform an examination of process variables in alkaline papermaking. In examining the effects of turbulence, they found that increased turbulence resulted in poorer AKD retention, though limited turbulence increased AKD retention when PPE was utilized. Retention increased as the AKD addition rate was increased up to 0.8%, and sizing was found to increase as the AKD was varied up to 0.6%. The optimum level of PPE was found to be 0.5-0.7%. This level yielded the highest AKD retention and sizing. Variations in beating the pulp showed that more heavily beaten pulps were better sized and retained more AKD.

The effects of alum on the AKD system were examined. AKD retention was found to be highest when 0.8% alum was used. Sizing was harmed by alum unless PPE was present. In the company of PPE, sizing was unaffected by alum.

Lindstrom and Soderberg[42] showed that AKD emulsion particles in an AKD-cationic starch emulsion have a net cationic charge within the pH range of 3-10, with the cationic character decreasing as the pH increases.

In examining retention aids, cationic polyelectrolytes were found to be more effective than cationic starch. Additionally, the use of deionized water yielded retention superior to that found with tap water.

An increasing pH was determined to lower AKD retention when polyelectrolytes were used. Salts and calcium lignosulfonates were also found to lower AKD retention.

High consistency pulps produced better AKD retention than low consistency pulps, and turbulence was detrimental to AKD retention.

Lindstrom and Soderberg found that polyelectrolytes decrease sizing when used at a given AKD reaction level compared to when they are not used. Additionally, white water circulation was found to decrease the sizing level, and extractives were determined to decrease the retained and reacted AKD.

Summary of the AKD Literature

The sources cited above illustrate the disagreement concerning the AKD sizing mechanism, and the complicated nature of AKD sizing.

There is no published direct proof of an AKD-cellulose esterification reaction in an aqueous papermaking system. The only proof of such an esterification reaction that has been published is for organic solvent systems.

There has been some evidence of hydrogen bonding between cellulose and AKD reported. Additionally, evidence of AKD migration has been reported by some

authors, which would suggest that the migrating material is not chemically bound to the pulp.

Most analyses of the reaction mechanism in the AKD system have been performed with infrared spectrometric techniques, seeking direct evidence of an esterification reaction. Because the sizing agent addition rate in an alkaline system is small, such analytical techniques, as well as others, are strained in examining alkaline systems.

The relation of AKD sizing to drying has generally shown that additional heating, through either increased drying temperatures or drying times, results in an improved sizing response.

ASA: LITERATURE REVIEW OF FACTORS AFFECTING SIZING

Wasser[43] examined ASA emulsions and ASA sized sheets. It was suggested that ASA emulsion hydrolysis was (1) proportional to temperature and pH and (2) inversely proportional to ASA particle size. It was suggested that the temperature and pH effects were of most importance.

Using sheets treated with ASA in toluene and oven dried, Wasser reported that the sizing development was proportional to temperature. Using ASA sized handsheets and drum drying, Wasser reported sizing was proportional to pH.

Wasser used sheets treated with ASA in toluene and air dried to assess post-curing effects. The sheets were either stored (1) in a desiccator or (2) at 73°F and 50% relative humidity. The sheets stored in the desiccator developed sizing. The sheets stored at 73°F and 50% relative humidity developed, and then lost, sizing. Wasser suggested there was a competition between the ASA reaction

with cellulose and the ASA reaction with water. It was theorized that storing the sheets in a desiccator eliminated the hydrolysis reaction. The sheets not stored in a desiccator could react with water to form the ASA hydrolysis product, which Wasser suggested was a desizing agent.

REACTIONS OF MATERIALS RELATED TO ASA

In an extensive series of reports, Cuculo, et al.,[44-48] demonstrated that succinic acid derivatives and the acid itself could be reacted with cellulosic materials to form an ester bond. The substrates included rayon, cotton, and wood pulp. The derivative used most often was succinamic acid. Other agents included succinic anhydride combined with ammonium hydroxide, and, as noted above, succinic acid. In some cases catalytic materials were also used.

The substrates were soaked in aqueous solutions of the agents, drained, and baked at temperatures usually exceeding 150°C. Degrees of substitution and carboxyl contents of the products were determined.

Verification of the products' ester structures was obtained using IR spectrometry of potassium bromide pellets. IR verification was performed on succinamic acid, ammonium succinamate and N,N-diethylsuccinamic acid reacted products only.

INFRARED AND DIFFUSE REFLECTANCE INFRARED SPECTROMETRY

An infrared (IR) spectrum of a molecule is the result of many aspects of the molecule. Certain areas in the IR region are characteristic of specific functional groups, however. While within these areas similar functional groups may vary in position depending on the molecule, it is possible to identify a

functional group with reasonable certainty using a spectrum in conjunction with some fundamental knowledge.

The mid-IR region is of greatest use. This is the region from about 700-4000 cm^{-1}. Many functional groups such as alcohols, acids and esters are clearly displayed in this region.

When infrared radiation is absorbed by a molecule, vibrations within the molecule occur and a change in the dipole moment may result. Those bonds that are involved in a change in the dipole moment are displayed in an IR spectrum.

There are two types of vibrations that occur, stretching and bending. Stretching is the movement of atoms along a bond's axis that results in a change in the distance between the atoms. The movement must be nonsymmetrical to have significance in IR spectrometry. Stretching is the vibration that is of interest in this thesis.[49]

Infrared spectra may be generated from samples in the liquid, gaseous and solid states.

As solids, there are several methods of examination of a material available. Among these are encapsulation in potassium bromide pellets, the use of deposited films on salt plates, attenuated total reflectance (ATR), also called multiple internal reflectance (MIR), and diffuse reflectance infrared Fourier Transform spectrometry (DRIFTS).

In this thesis, use of deposited films and DRIFTS was made. The deposition of sample films directly on, or from a solvent onto, a salt plate is simple and requires no explanation; DRIFTS is more complicated.

DRIFTS is a method for examining materials prone to reflect radiation diffusely. While specular reflection components from the sample surface, which have equal incidence and reflectance angles, may be present, diffuse reflection may also be present and involves penetration of radiation into the sample material. Randomly directed reflections that emerge from the material are diffuse reflections.[50]

Quantitation using DRIFTS is often discussed in the literature, and Kubelka-Munk theory is usually invoked to describe the relationship between sample concentration and diffuse reflectance. While the theory is applicable in some cases, in examining paper or pulp samples the theory would not be easily applicable.

While subtractions utilizing diffuse reflectance spectra can be performed successfully, and are useful qualitatively, direct quantitation using DRIFTS is questionable.[51] While direct quantitation would be unlikely in paper or pulp samples, DRIFTS is extremely useful in examining such samples because it allows direct examinations with no sample preparation. Further, the spectra obtained by DRIFTS from cellulosic samples are reasonably easy to interpret.

PRESENTATION OF THE PROBLEM AND THESIS OBJECTIVES

While alkaline sizes have been used for the past several decades, there is uncertainty concerning the mechanism by which these materials function. Though the mechanism should be simple, direct evidence for what occurs is complicated by the small amounts of sizing material involved, typically under 0.5%. This makes instrumental analysis difficult. While some work has been performed in this area already, the authors disagree to some extent, and a clear mechanism has not been proven to date.[23-25,28-32,34,36] Additionally, most work performed has been with alkyl ketene dimers, with a four-membered lactone being the functional group. The work detailed in this thesis involves alkenyl succinic anhydride, with a five-membered cyclic anhydride being the functional group. The chemical and physical differences of these two materials, though they are both reported to act through similar mechanisms, could be important to an elucidation of the alkaline sizing mechanism.

The purposes of this thesis were to clarify the mechanism involved in ASA sizing and to characterize the sizing results as influenced by several factors. Further, the potential for ASA migration through the sheet was to be examined, as AKD migration has been suggested to be incompatible with esterification. The above purposes constituted the three phases of this thesis.

Specifically, the objectives of this work were to (1) determine whether an ester bond is formed between ASA and cellulosic hydroxyl groups and (2) determine the effects of the time of drying, the temperature of drying, and the conditioning time on the sizing level.

APPROACH

THE SYSTEM

A system simulating a papermaking environment as closely as possible was considered desirable and a handsheet study was considered most reasonable. This allowed reproducibility and a variety of conditions to be tested. Drying was performed in a convection oven because the equipment allowed a range of temperatures to be tested, conditions were reproducible, and the oven was readily available. Some contact drying was performed as well.

MATERIALS

A commercial cotton linters pulp was chosen because of cotton's high cellulosic content. Cotton is reported to be about 85-90% cellulose. Further, cotton contains only about 1% extractives, is essentially free of hemicelluloses, and is low in lignin, having a lignin content of about 1%. The remainder of cotton is composed of small quantities (< 2%) of ash, protein and pentosans. The precise chemical composition reported varies with the sample and the methods of determination.[9,52] The chemical composition of cotton was considered advantageous, as the high level of cellulose and the low levels of other materials made the ASA-cellulose esterification more likely and side reactions of ASA less likely.

A commercial ASA was utilized along with a cationic polymer. This cationic polymer was used as a retention aid, since the starch supplied with the ASA was found to react with the ASA. Use of the polymer allowed the retention aid addition level to be small and decreased the potential for an ASA-retention aid reaction. ASA emulsions were produced in water without benefit of an emulsifying

agent because the supplied emulsifying agent was found to react with ASA. The starch and the emulsifying agent had to be eliminated from the system because it was desired that the only possible reactions be between ASA and cellulose, or water. A description of the experimental work performed in examining the reaction of the emulsifying agent and the starch with ASA may be found in Appendix I.

ANALYSIS AND TESTING

An infrared spectrometric examination for the ester was used because it was considered the most direct and useful functional group analysis.

In addition to the papermaking system employed, a more traditional organic reaction was also used to provide useful information concerning the ester IR peak position. Further, this provided indications of the likelihood of observing the ester under the less favorable papermaking conditions.

Testing was limited to DRIFTS evaluation of samples and Hercules Size Tests of handsheets. Some transmission IR spectrometry of sheet extracts and raw materials was also performed.

DRIFTS was utilized because it allowed direct examination of samples that would yield precisely the information desired (i.e., whether the ASA-cellulose ester was formed). While only a semiquantitative method, the trends in reaction were adequately shown for the purposes of this thesis.

The ASA would be expected to display IR carbonyl stretching peaks at about 1782 and 1865 cm^{-1}, and the ASA-cellulose ester would be expected to display a carbonyl stretching peak at between 1735 and 1750 cm^{-1}. No other materials used in this thesis could produce a peak in the IR ester region. The carboxylic acid

resulting from ASA hydrolysis, or in conjunction with esterification, would display a carbonyl stretching peak at between 1706 and 1720 cm^{-1}. Salts of the carboxylic acid would display a peak at between 1550 and 1650 cm^{-1}.[49]

The Hercules Size Test was chosen because it is a commonly used method that allows reasonably rapid and simple testing, with good reproducibility and the ability to adapt experimental variables to different sample conditions. The reflectance endpoint and the formic acid content of the ink may be varied widely.

Sheet extractions were performed in toluene because it is a good solvent for the materials involved in this thesis.

EXPERIMENTATION

In the first phase of this thesis, in addition to determining by DRIFTS whether an ASA-cellulose ester could be formed, an examination of the ability of the ASA hydrolysis product to promote sizing was performed by adding the hydrolysis product directly to sheets. Further, sheets prepared with delayed pressing and drying, such that hydrolysis of the ASA would be increased, were made. Size tests, comparing these sheets to sheets prepared with ASA that were immediately pressed and dried to minimize hydrolysis, followed.

The second phase of this thesis is straightforward and involved an examination of sizing and reaction while varying conditioning time, drying time, and drying temperature. DRIFTS and size tests were used in this phase.

In the third phase of this thesis, laminated handsheets were used to examine ASA migration. This method was chosen because it would yield the information

desired and allow reasonably simple measurements that would describe the potential for ASA migration in a sheet of paper. The layers of the handsheets were examined by DRIFTS, transmission IR spectrometry of sheet extracts, and size tests.

EXPERIMENTAL MATERIALS, EQUIPMENT, AND PROCEDURES

MATERIALS

A second cut, cotton linters dry lap pulp was donated by Alpha Cellulose Corporation and prepared as described in Appendix II.

The ASA was obtained from National Starch and Chemical Corporation under the product name of Fibran 68. Analysis of the ASA is described in Appendix III.

Poly(1,2-dimethyl-5-vinylpyridinium bromide) (DMVPB) was used as a retention aid. The polymer was synthesized by Eggert[53] and has a weight average molecular weight of 10^6. The repeating unit of DMVPB is shown in Fig. 7. It should be noted that while DMVPB was used to retain ASA, retention of fines through use of the polymer would also be anticipated.

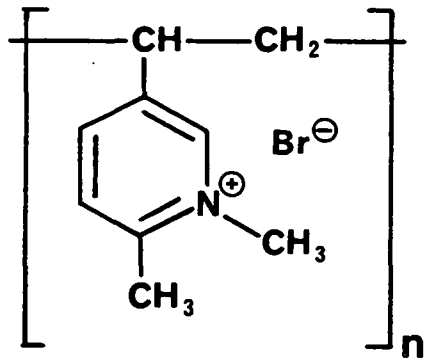


Figure 7. DMVPB.

EQUIPMENT

To prevent polymer adsorption onto the glassware, all glassware containing the polymer DMVPB was treated with a 1% solution of polyethylene glycol overnight and rinsed repeatedly with distilled water. Following this, the glassware

was treated with the polymer overnight, rinsed thoroughly with distilled water, and then used.

Pulp was dispersed before use in a British Disintegrator described in TAPPI Standard T 205 om-81.[54] Handsheets were made in a British handsheet mold described in TAPPI Standard T 205 om-81.[54] ASA and ASA hydrolysis product emulsions were prepared in an Eberbach 8590 mixer mounted on a Waring Blendor base. Handsheets were oven dried in a Precision Scientific model 625 convection oven, or contact dried on a stainless steel steam drum, having a 105°C surface temperature, under a press felt. Size tests were performed on a Hercules Sizing Tester made by Hercules, Inc.[55] All infrared spectrometry work was performed on a Nicolet Instrument Corporation model 7199 FT-IR spectrometer. DRIFTS was performed using a Harrick's Praying Mantis unit. Transmission spectra were run on sodium chloride plates. Gas chromatography/mass spectrometry (GC/MS) was performed on an OV-17 column and a Hewlett-Packard model 5985 mass spectrometer.

PROCEDURES

Reaction of ASA in N,N-Dimethylformamide With Cotton Linters

ASA (25 mL) was reacted with 3.5 oven dry grams of cotton linters in 100 mL of N,N-dimethylformamide using 0.3 mL of triethylamine as a catalyst. The N,N-dimethylformamide was used as an ASA solvent to provide uniform distribution of the ASA around the cotton linters. The mixture was refluxed to 60°C with a magnetic stirrer providing mixing, whereupon the ASA was added. Heating continued to 85°C, where the mixture remained for 1.25 hours. After cooling overnight, the fiber was filtered, extracted in a Soxhlet extraction apparatus using toluene for 20 hours, filtered again, air dried, and then oven dried at 105°C for 3 hours to remove N,N-dimethylformamide. The N,N-dimethylformamide

was dried before use with Davison grade 564 3 Å molecular sieves. A drying tube was attached to the condenser during the reaction.

Handsheet Production

Handsheets were produced using the equipment described above in accordance with TAPPI Standard T 205 om-81,[54] with exceptions as noted below. It should be noted here that all references in this thesis to amounts of chemicals contained in sheets refer to addition levels, and that all addition levels are on an oven dried fiber basis. The pulp was soaked in distilled water for 24 hours and dispersed at 1.2% consistency in a British Disintegrator for 90 seconds. The pulp was diluted to 1% consistency and adjusted to a pH of 7.5. An amount of pulp appropriate for a single handsheet was then placed in a 250 mL glass beaker. The mold was filled with deionized water and its pH adjusted to 7.5. Any deviations from a pH of 7.5 during formation are noted where appropriate. If an emulsion was used, it was added to the pulp at this point under gentle stirring supplied by a Lightnin' Mixer and retained for 2 minutes. If DMVPB was added, it was gently mixed into the pulp next, and retained 2 minutes.

The addition rate of DMVPB when it was used was 0.15% based on pulp. The addition rate of DMVPB was determined by varying the DMVPB addition rate from 0.05-0.25% in sheets to which 10% ASA was added. Examining these sheets by DRIFTS at ca. 1785 cm^{-1} for the ASA peak showed that 0.15% DMVPB provided the maximum ASA retention, while avoiding overdosage of the polymer.

Any deviations from the above addition order are as noted where relevant.

The pulp was then added to the mold, the sheets were formed, pressed immediately, unless otherwise noted, and oven dried immediately for one hour at

105°C, unless otherwise noted. Sheets were made at a weight of 1.8 oven dry grams each, unless otherwise noted. Sulfuric acid (0.05N) and 0.1N sodium hydroxide were used for pH adjustment.

Emulsions were formed in the mixer noted previously. Emulsification was for 45 seconds on the high speed setting. ASA emulsions were composed of 1.5 grams of ASA added to 98.5 grams of distilled water. Fresh emulsions were prepared for each sheet and used immediately, unless otherwise noted.

Hydrolysis Product Sheets

Sheets formed with the ASA hydrolysis product utilized hydrolysis product formed from 10 grams of ASA and 1.5 grams of distilled water. The two materials were mixed by hand intermittently for three days. This resulted in complete hydrolysis of the ASA, as determined by examination of an infrared transmission spectrum of the mixture for ASA and hydrolysis product bands. Emulsions of the hydrolysis product were formed in distilled water using the equipment and procedures described for ASA emulsification. Hydrolysis product emulsions were formed at from 1.6 to 2.56% hydrolysis product.

Other procedures for sheets containing the hydrolysis product were similar to those mentioned for sheets containing ASA. In some cases alum, or DMVPB, was added. While the normal sheet formation consistency was about 0.026%, some hydrolysis product sheets were made at 1-2% consistency to increase hydrolysis product retention. These sheets contained from 1-43% hydrolysis product, and of these, some contained 0.15% DMVPB. Some sheets were also formed at a pH of 4.0. Variations in hydrolysis product sheet production are shown in Appendix IV along with DRIFTS spectra showing that the hydrolysis product was retained in high consistency sheets. Some sheets containing 0.25-0.5% ASA and 0.15% DMVPB were

also made at 1% consistency to compare to the 1-2% consistency hydrolysis product sheets.

Conditioning and Sample Treatment

Conditioning of samples was at 72°F and 50% relative humidity for the times specified on relevant figures and tables. Sheet extractions in toluene were performed in a Soxhlet extraction apparatus for 14-18 hours.

Hercules Size Tests

Size tests were run on the Hercules Sizing Tester using 10% formic acid ink and an 80% reflectance end point, unless otherwise noted. The test ink was applied to the felt side of the sample sheet. The test has two variables, formic acid content of the ink and the reflectance end point. Lowering the formic acid content of the ink or lowering the reflectance end point causes the size test to be larger. Increasing the formic acid content of the ink or increasing the reflectance end point causes the size test to be smaller. If the sample is strongly sized, a high formic acid content ink and/or a high reflectance endpoint is used to obtain size tests of reasonable length, while a sample that is weakly sized would require an ink with a lower formic acid content and/or a lower reflectance end point. The size test is shown in Fig. 8. Operation of the tester and preparation of the ink is described in the Hercules Sizing Tester manual.[55]

Spectrometric Techniques

All spectra were obtained at 2 cm^{-1} resolution and were baseline corrected from 400-4000 cm^{-1}. Diffuse reflectance spectra were obtained from 500 scans (2 runs of 250 scans that were coadded). All samples were examined on the felt side. Powdered potassium chloride was used as a background material.

Subtractive spectral data were obtained by subtracting out the spectrum of a sheet of pure cotton linters from the spectrum of the sample of interest over the range of 1350-2000 cm^{-1}. Baseline correction of subtracted spectra was from 1685 to 1900 cm^{-1}.

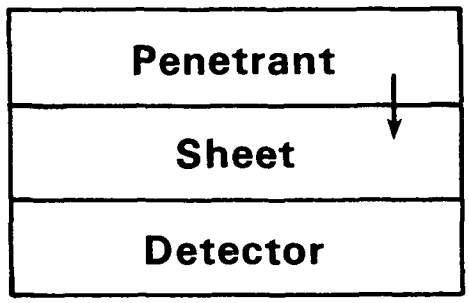


Figure 8. The Hercules Size test showing the direction of penetration.

Diffuse reflectance and transmission spectra were measured in absorbance units. It should be noted that the concentration of a species is proportional to the absorbance of the IR peaks attributable to the species.

Semiquantitative DRIFTS measurements of sheet samples were obtained from subtraction spectra. Measurements were made in absorbance units of the ASA carbonyl stretching peaks at ca. 1785 and 1865 cm^{-1}, the carboxylic acid carbonyl stretching peak resulting from formation of the ASA hydrolysis product, or the acid formed in conjunction with esterification at ca. 1710 cm^{-1}, and the ester carbonyl stretching peak at ca. 1730 cm^{-1}. It should be noted that the ester and acid peaks mentioned above are shoulders on each other. Thus, an increase or decrease in the intensity of one peak will affect the intensity of the other peak. Additionally, it should be noted that distinguishing between the peak at 1710 cm^{-1} due to the acid formed in conjunction with esterification, and the acid peak due to the ASA hydrolysis product, is not possible.

Transmission IR spectra were obtained from 100 scans, and were either produced by evaporating solvent off the sample, or by applying the material directly to a salt plate.

Investigation of Cellulose Oxidation During Drying

To determine whether oven drying could cause cellulose oxidation that might complicate the IR ester region, samples were prepared and dried by either oven drying or vacuum drying. A DRIFTS examination and comparison followed this preparation. Vacuum dried sheets would not be expected to display as much evidence of oxidation as oven dried sheets.

No evidence was found of cellulose oxidation during oven drying. Diffuse reflectance IR spectra of oven dried sheets and vacuum dried sheets were indistinguishable from one another.

Reaction of Ethanol with ASA

Absolute ethanol (0.9 gram) was mixed intermittently by hand for three days with 2.512 grams of the ASA in a glass beaker to form the ethanol-ASA ester-acid.

Laminated Sheet Production

Laminated sheets were prepared by forming sheets as described above, except that one layer without ASA or DMVPB was made at 1.0 oven dry gram per sheet. The 1.0 gram layer (Layer 2) was made first without pressing or drying, and stored in plastic wrap. Layers 3-5 were made next and did not contain ASA or DMVPB. These layers weighed 1.8 oven dry grams per sheet and were for testing. Layers 3 and 5 were pressed per TAPPI Standard T 205 om-81,[54] and placed in plastic wrap. Layer 4 was not pressed or dried, but was stored in plastic wrap.

Layer 1 was made last at 1.8 oven dry grams per sheet and contained 1.5% ASA, unless otherwise noted, and 0.15% DMVPB. Layer 1 was pressed in accordance with TAPPI Standard T 205 om-81, but not dried.[54] Sheets that were not pressed were treated this way to retain enough moisture such that adhesion of the sheets to each other would develop during drying without pressing the sheets together.

Laminations were made as soon as Layer 1 was prepared to prevent ASA hydrolysis. The felt side of Layer 1 was laid on the felt side of Layer 2, the felt side of Layer 3 was laid on the wire side of Layer 2, the felt side of Layer 4 was laid on the wire side of Layer 3, and the felt side of Layer 5 was laid on the wire side of Layer 4. Layer 2 served as a barrier to prevent physical contact between Layer 1 and Layer 3. No pressing was used to bond the layers together. The layers were then dried together with the wire side of Layer 1 in contact with the dryer (steam drum at 7.5 psig). A press felt was placed over the sheets during drying, the duration of which is noted in relevant figures and tables. The laminated sheet is shown in Fig. 9 during drying. The resulting laminated sheet was lightly bonded together and easily separable by hand. Sheets remained laminated during conditioning, unless otherwise noted. In some laminated sheets only Layers 1-3 were used. The above procedure is correct for these sheets as well.

Extraction of Laminated Sheets

Toluene extracts of the layers of laminated sheets were obtained using a Soxhlet extraction apparatus for 14-18 hours, as previously mentioned. The resulting extract was concentrated by simple distillation to 2.5-3.0 grams. The concentrate was then evaporated to dryness on a sodium chloride plate and examined by transmission IR spectrometry.

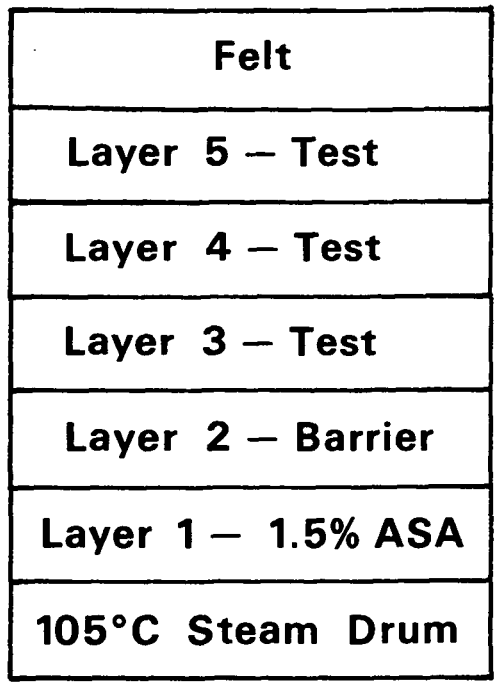


Figure 9. A laminated sheet during drying.

RESULTS

The following section presents the results of the experimental work performed in this thesis. A discussion of these results is presented after this section.

INFRARED PEAK POSITIONS OF MATERIALS

To determine precisely where IR peaks of interest of the materials being used in this thesis should appear, transmission spectra of the ASA, the ASA hydrolysis product, and the sodium salt of the ASA hydrolysis product were produced. These are shown in Fig. 10, 11 and 12. Peaks from ASA were observed at about 1785 and 1865 cm^{-1}, and a peak from the ASA hydrolysis product was observed at about 1710 cm^{-1}. A peak from the ASA hydrolysis product salt was visible at about 1565 cm^{-1}. Additionally, a diffuse reflectance spectrum of DMVPB was produced. This spectrum is shown in Fig. 13.

It should be noted here that general peak positions are used for species throughout this thesis, except in some cases where reference to a specific spectrum is being made. Thus, 1785 cm^{-1} and 1865 cm^{-1} are the general peak positions for ASA, 1730 cm^{-1} is the general peak position for the ester, and 1710 cm^{-1} is the general peak position for the acid. The precise peak positions may vary by 2-4 cm^{-1} in either direction from the general peak positions noted above.

DETERMINATION OF ESTERIFICATION

The first phase of this thesis was designed to determine whether an esterification reaction between ASA and cellulosic hydroxyl groups could occur.

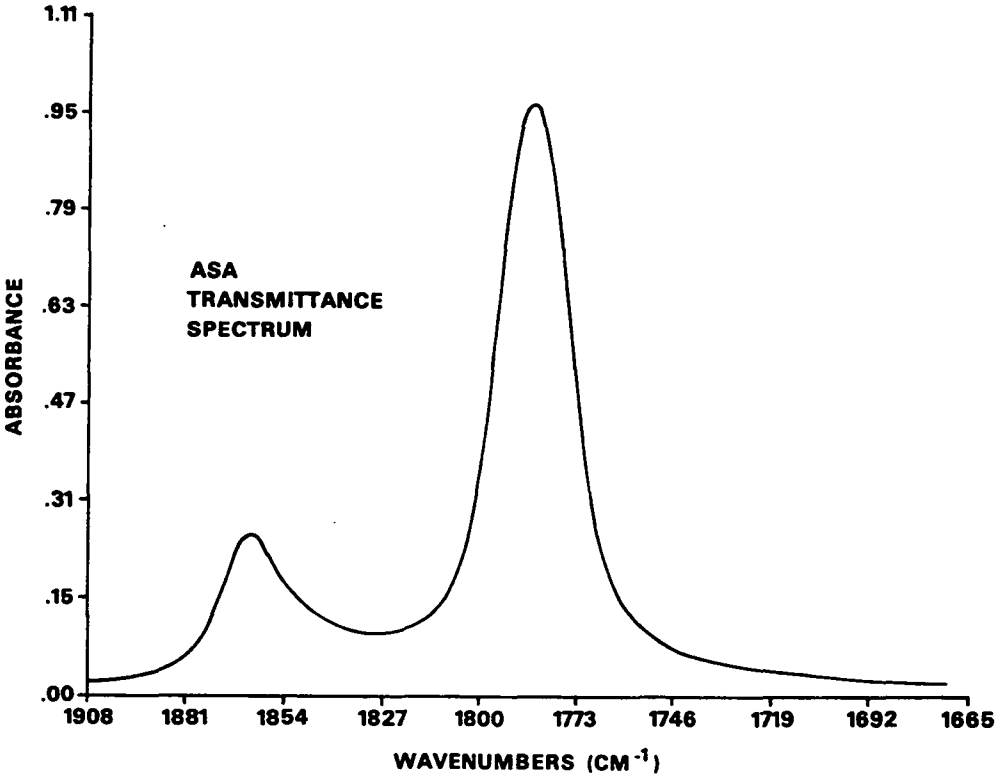


Figure 10. ASA IR transmission spectrum.

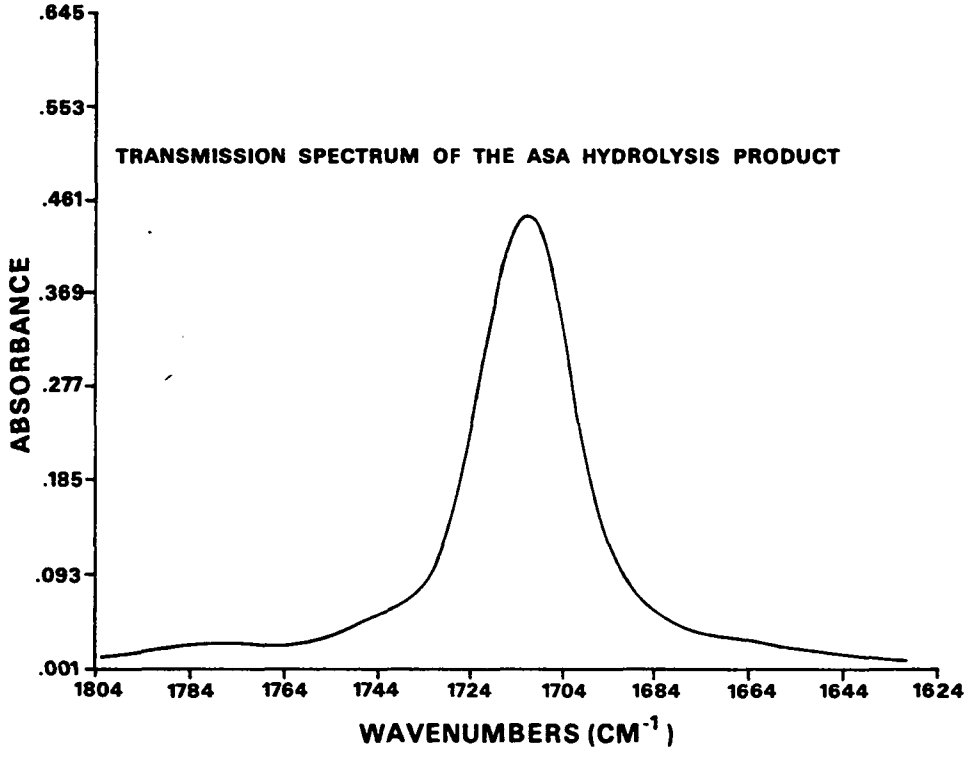


Figure 11. ASA hydrolysis product IR transmission spectrum.

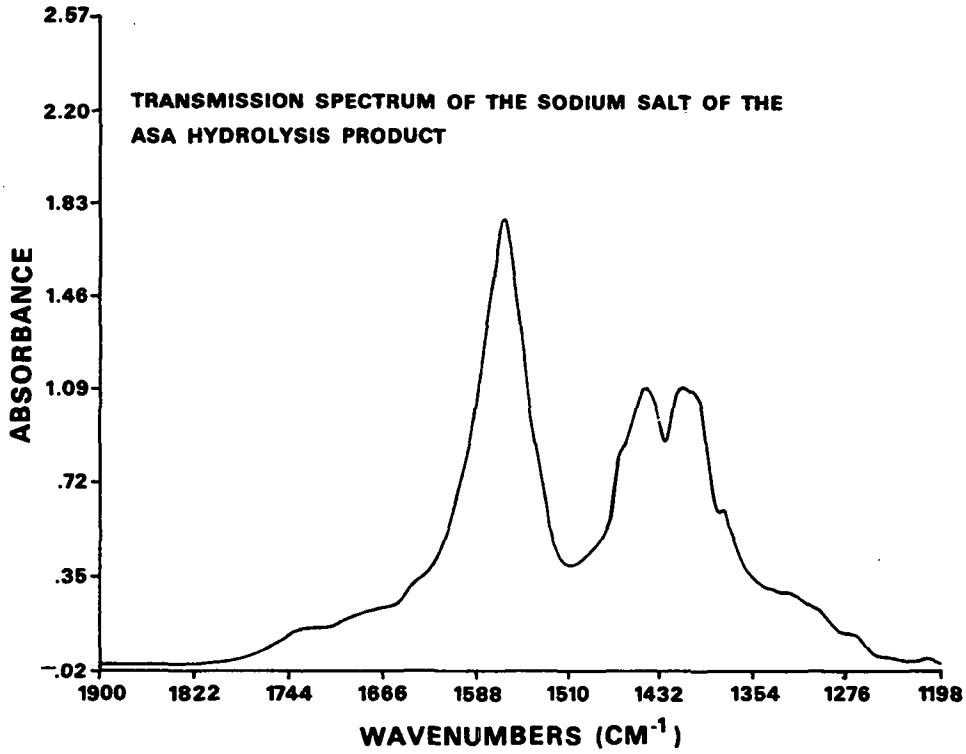


Figure 12. ASA hydrolysis product sodium salt IR transmission spectrum.

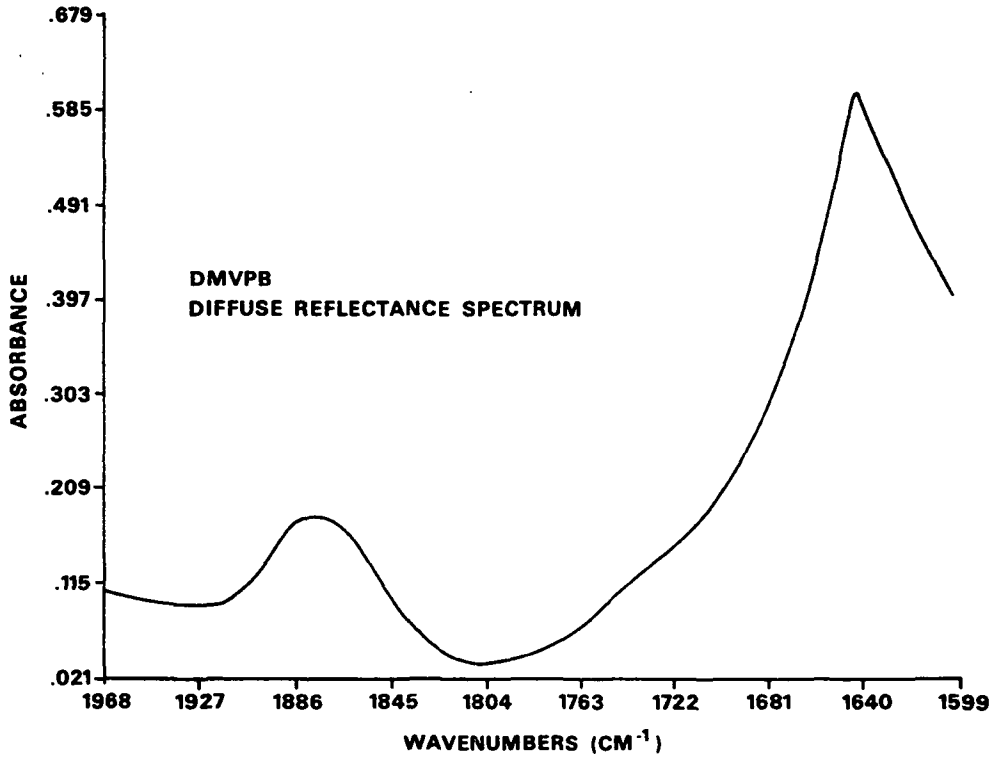


Figure 13. DMVPB diffuse reflectance IR spectrum.

In an organic solvent system, evidence for esterification was observed. This is seen in Fig. 14, where cotton linters before and after reaction are compared. A broad IR peak at ca. 1732 cm^{-1} can be taken as an indication of esterification in N,N-dimethylformamide, a situation dissimilar to papermaking conditions. The broad nature of this peak can easily be attributed to overlapping ester and acid peaks that arise simultaneously from the ASA-cellulose reaction, as shown in Fig. 3.

Under papermaking conditions an ester was also visible in an IR spectrum at approximately 1730 cm^{-1}. This is shown in Fig. 15. Acid groups were somewhat less evident, but clearly present at about 1714 cm^{-1}. Additionally, unconsumed ASA was clearly evident at 1785 and 1865 cm^{-1}. Though levels of ASA greater than typically used in a paper mill were added to the pulp (1.5%), there is no reason to suspect a similar reaction would not occur at more typical levels of ASA usage (0.1-0.25%).[56] The increased levels of ASA were necessary to make the ester readily visible by DRIFTS.

No IR evidence was observed of the presence of the salt of the ASA hydrolysis product's carboxylic acid, or the salt of the acid produced in conjunction with esterification. A peak at about 1565 cm^{-1} would have been observed if the carboxylate anion of either of the above species was present; no such peak was observed.

EVALUATION OF THE HYDROLYSIS PRODUCT AS A SIZING AGENT

Sheets made with the ASA hydrolysis product, as described in Appendix IV, displayed no sizing using 1% formic acid ink and a 65% reflectance endpoint. This was true for sheets formed at normal (0.026%), or higher consistencies (1-2%). In contrast, sheets made with 0.5% ASA and 0.15% DMVPB at normal, or 1%,

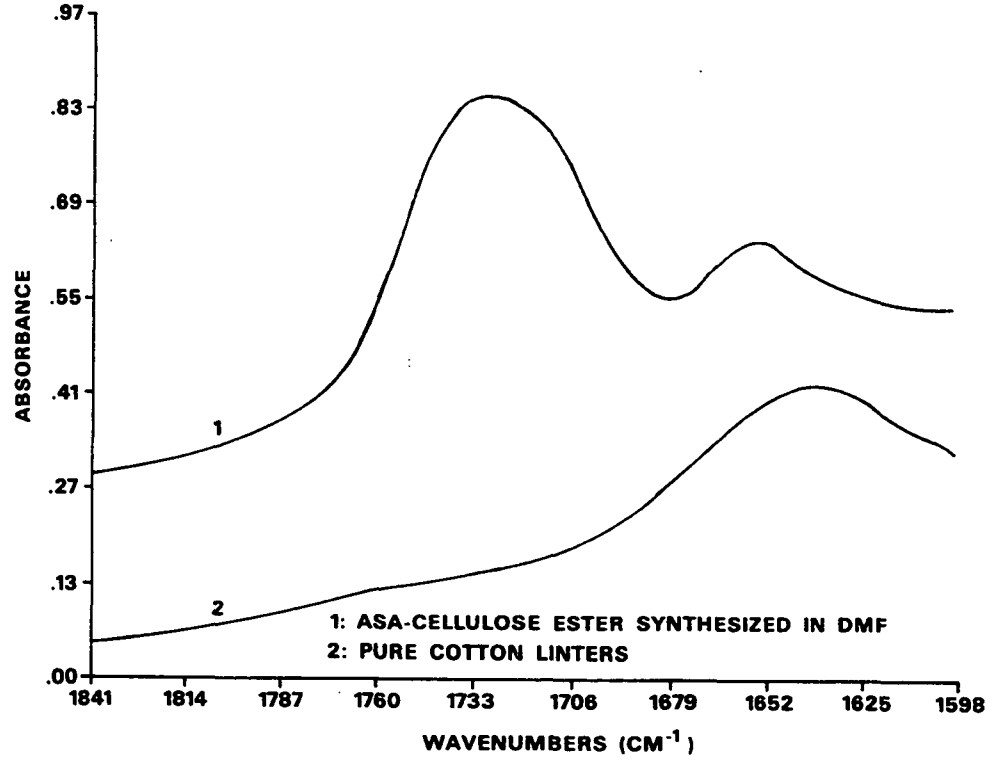


Figure 14. Diffuse reflectance IR spectra of cotton linters before and after reaction with ASA.

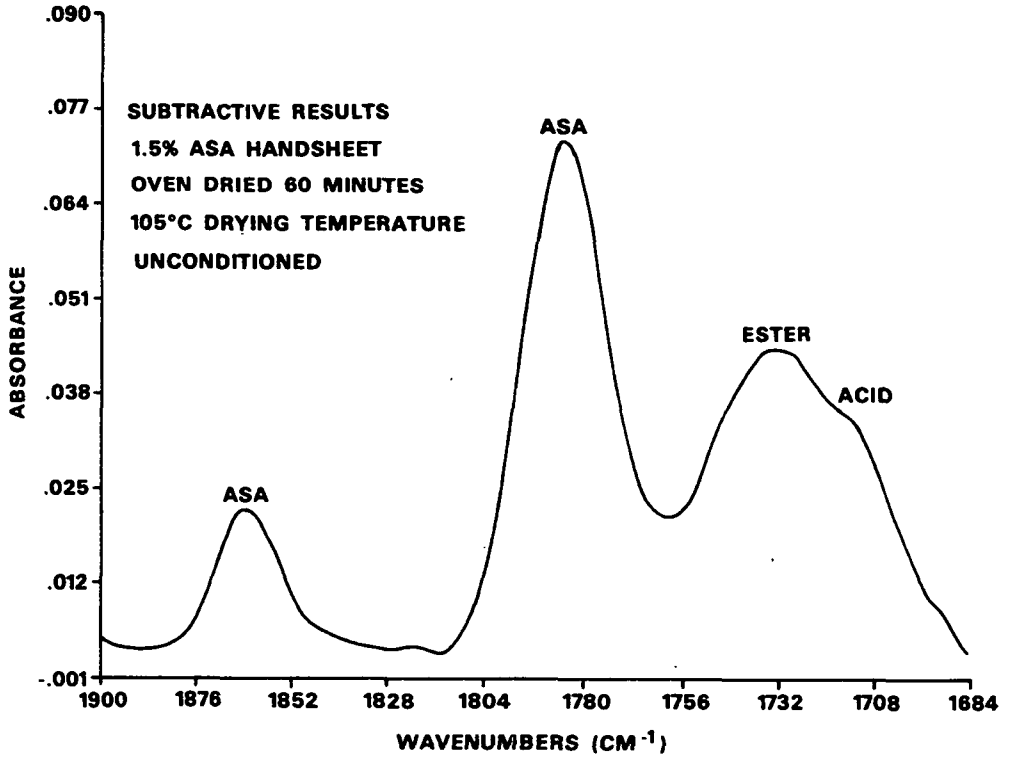


Figure 15. Diffuse reflectance IR spectrum of a handsheet made with ASA.

consistency, displayed good sizing - in excess of 800 seconds using 10% formic acid ink and a 90% reflectance end point.

A sheet containing 0.5% ASA and 0.15% DMVPB, and prepared with 1 week of delayed pressing and drying to promote ASA hydrolysis displayed decreased sizing compared to a sheet containing the same materials prepared with immediate pressing and drying. This is shown in Table 1.

Table 1. Sizing results of a sheet prepared with delayed pressing and drying versus sizing results of a sheet prepared with immediate pressing and drying.

Pressing and Drying	Reflectance End Point, %	Formic Acid Ink, %	Hercules Size Test, sec
Immediate	90	10	800+
Delayed	65	1	73

EFFECTS OF EMULSION AGING AND SHEET MOISTURE

Prior to beginning the second phase of this thesis it was necessary to determine the effect of ASA emulsion aging and short term aging of unpressed and undried ASA containing sheets on sizing. Using one ASA emulsion for six sheets and delaying pressing and drying until all six sheets were formed, it was found that sizing first decreased and then increased from the first sheet to the last. One hour was required to form all six sheets. The results are shown in Table 2. Due to these results, to subsequently obtain reproducible and comparable sizing results each sheet was made with a freshly prepared ASA emulsion that was used immediately after emulsification. Additionally, each sheet was immediately pressed and dried after formation.

Table 2. Sizing results from sheets made with an aged emulsion and delayed pressing and drying.

Sheet Order	Hercules Size Test, sec
1st	321
2nd	236
3rd	553
4th	611
5th	696
6th	720

EFFECTS OF DRYING VARIABLES ON SIZING

In the second phase of this thesis, one of the objectives was to characterize ASA sizing response under varied conditioning times, drying times, and drying temperatures. The complete data from this phase are presented in Appendix V. An ASA addition level of 0.15% was used in this phase, and the sheets also contained 0.15% DMVPB.

Drying Temperature

As the drying temperature was increased from 65 to 105°C, the sizing maximum was increased. Additionally, the rate of sizing development increased as the drying temperature increased. For a given time of drying, a sample dried at a higher temperature yielded a better sizing level than a sample dried at a lower temperature. These results are shown in Fig. 16.

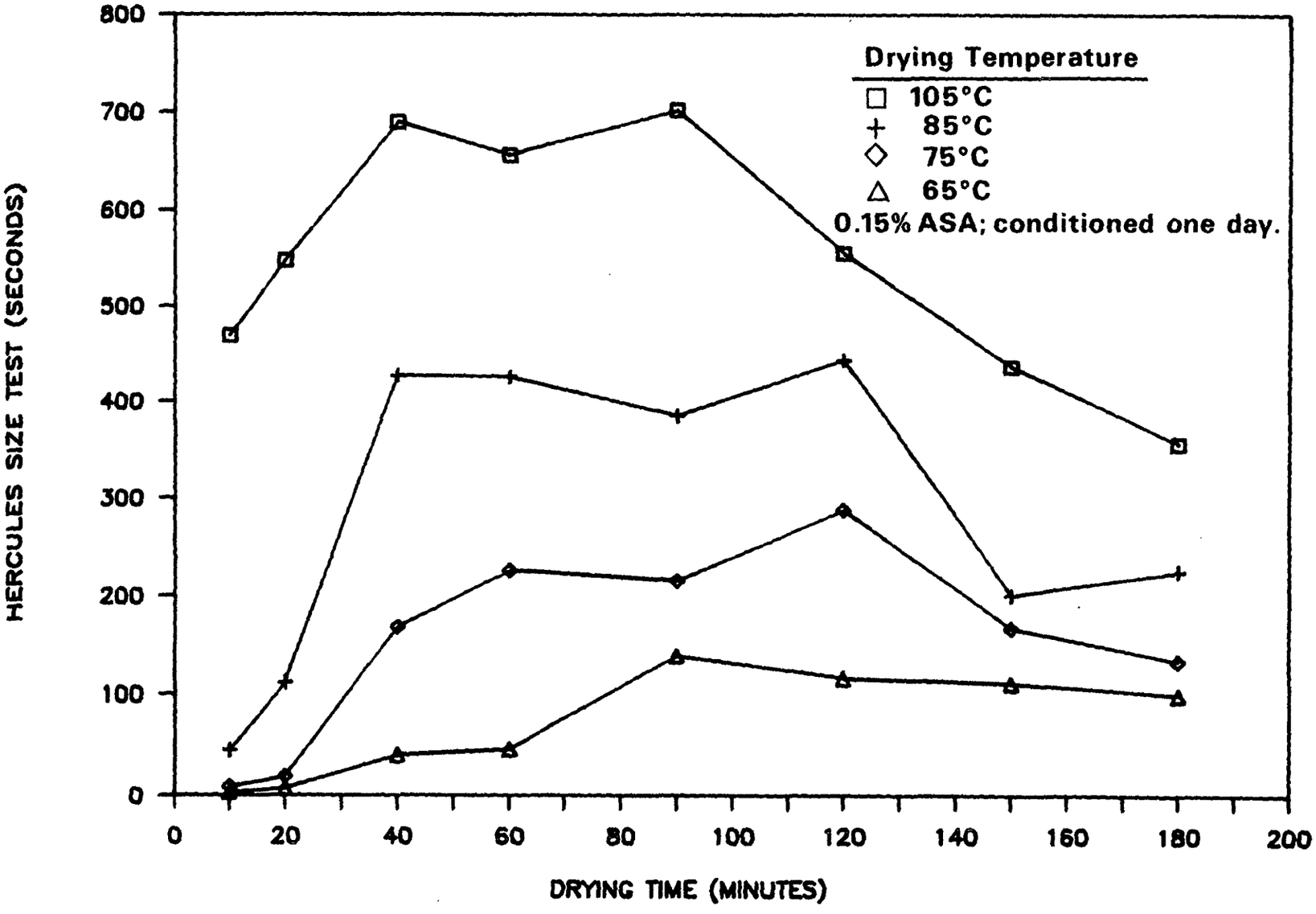


Figure 16. Hercules Size Tests of sheets dried at different temperatures for varying times.

Drying Time

As the drying time increased the sizing level increased to a maximum and then decreased at long drying times. This decrease was particularly noticeable in the 85 and 105°C drying temperature data when the sheets were conditioned. The extent and the rate of decrease was variable. These data are shown in Fig. 16.

Conditioning Time

In examining the influence of conditioning it was observed that sheets dried at 105°C for up to 60 minutes and conditioned for one day yielded sizing superior to sheets with similar drying times that were tested immediately after drying (i.e., with no conditioning). At drying temperatures of 75 and 85°C, the superior sizing of conditioned sheets compared to unconditioned sheets was observed up to drying times of 150 and 120 minutes, respectively. These data are shown in Fig. 17.

There were no conclusive differences in the sizing results when sheets conditioned for one day were compared to sheets conditioned for one week. This is apparent in Fig. 18.

Type of Drying

In comparing the sizing levels of sheets that were contact dried to those that were oven dried, results were similar except that contact dried sheets displayed no decrease in sizing at long drying times, as observed in oven dried sheets. This contrast is shown in Fig. 19 for sheets conditioned one day. The data are included in Appendix V in Table 9.

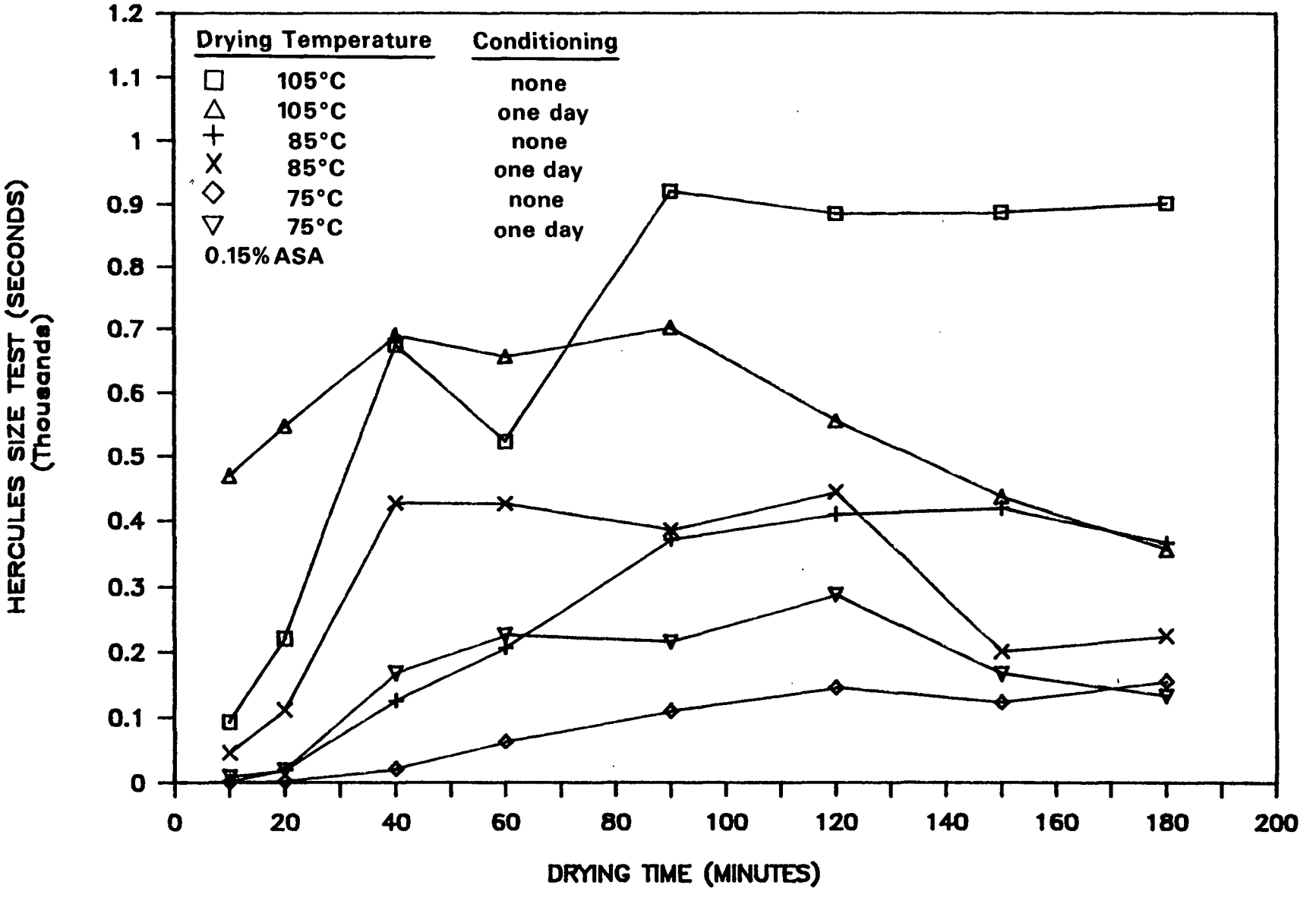


Figure 17. Hercules Size Tests of sheets dried at different temperatures for varying times with and without conditioning.

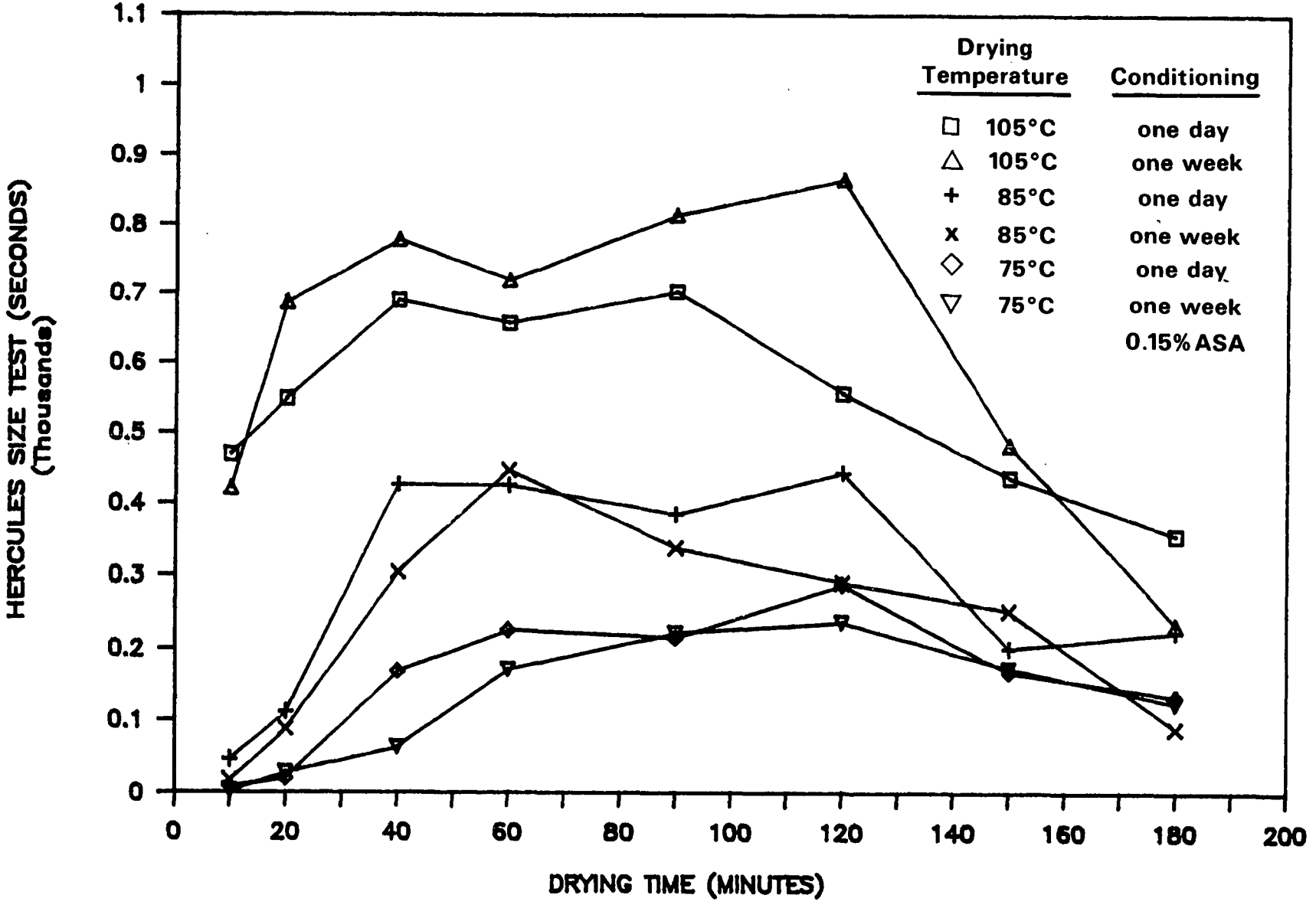


Figure 18. Hercules Size Tests of sheets dried at different temperatures for varying times with one day and one week of conditioning.

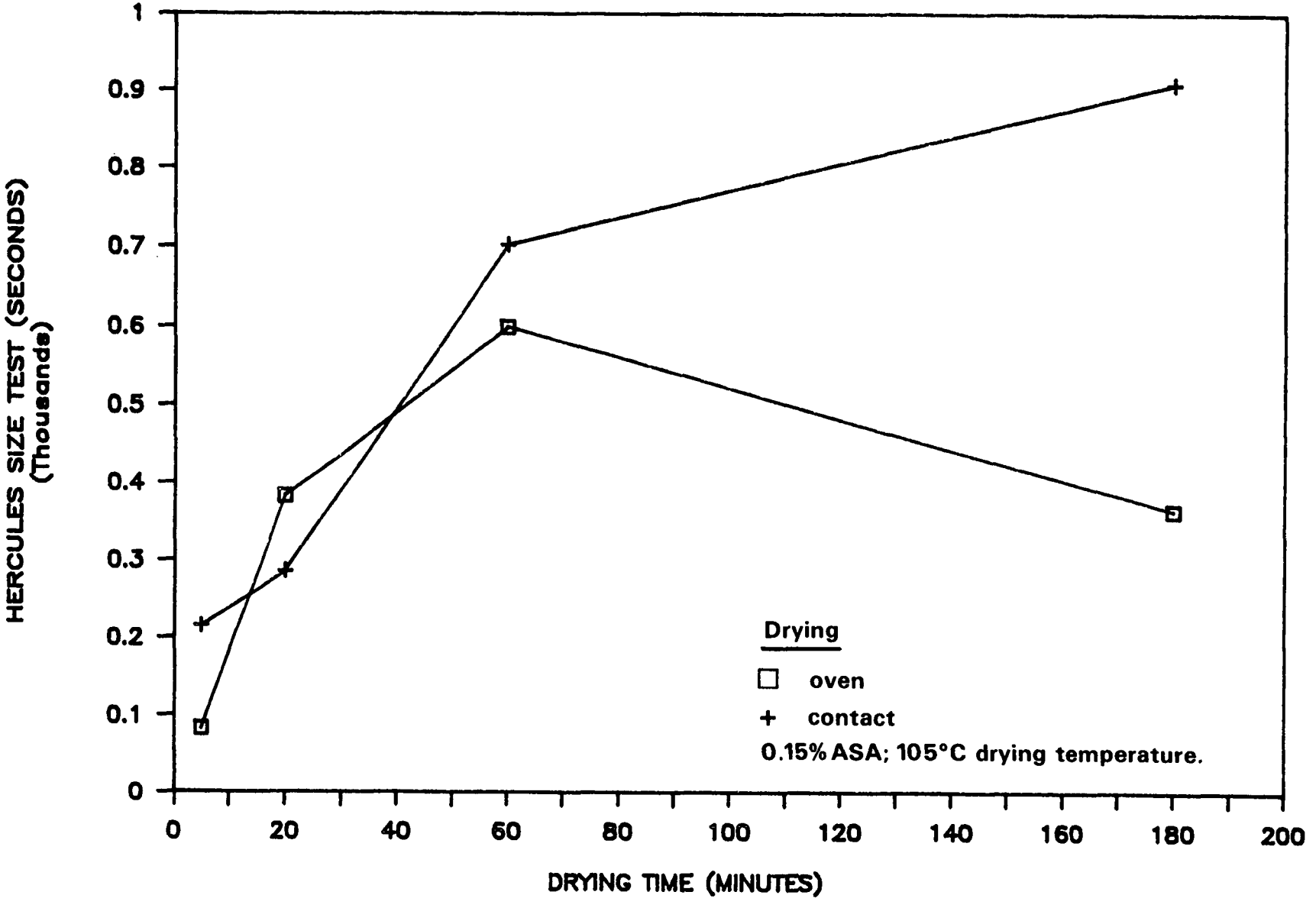


Figure 19. Hercules Size Tests of sheets made with ASA that were oven or contact dried.

PRECISION OF HERCULES SIZE TESTS

An analysis of the precision of the Hercules Size Test is presented in Appendix VI.

EFFECTS OF DRYING VARIABLES ON REACTION

An additional objective of the second phase of this thesis was to characterize the effects of the three variables mentioned above (conditioning time, drying time, drying temperature) on the esterification of ASA with cellulose. An addition level of 1.5% ASA was used to make the results discernible and the trends distinguishable by DRIFTS. The sheets also contained 0.15% DMVPB. The levels of ASA and the carboxylic acid were measured along with the ester levels in this portion of the work, as they were readily obtainable.

All data for this phase are located in Appendix VII. The clearest examples of common trends found in this portion of the second phase are shown in the following figures.

Reproducibility of these data was tested by making two identically prepared sheets, subjecting them to the subtraction technique described previously, and comparing the results. The results are shown in Fig. 20. The data for Fig. 20 are included in Tables 23 and 35 of Appendix VII. The results suggest that good reproducibility is possible despite the manipulation of data during subtractions.

Drying Temperature

It should be noted that higher drying temperatures seemed to yield clearer data trends than lower drying temperatures.

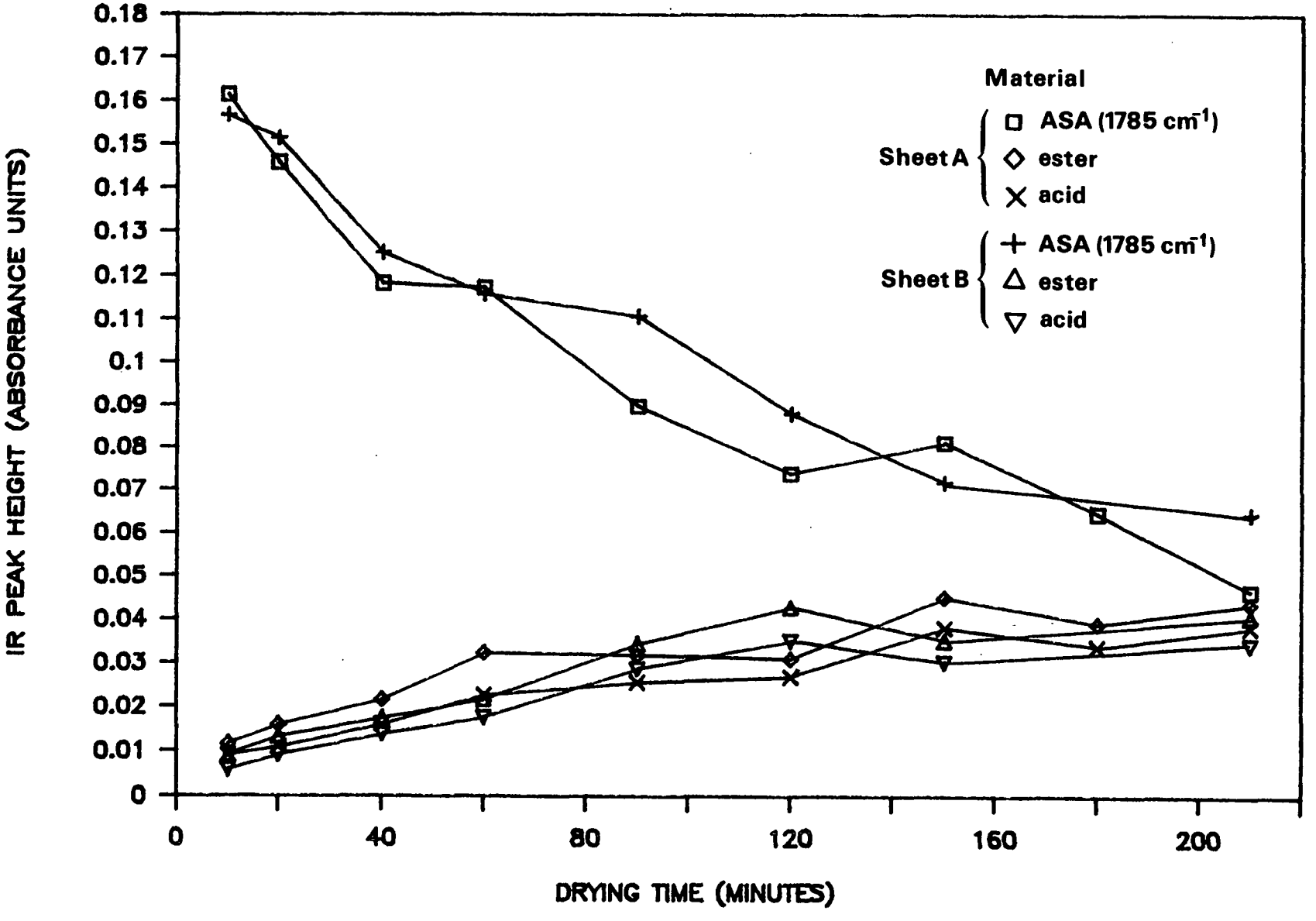


Figure 20. Comparison of the DRIFTS peak heights, by subtraction, of two sheets during drying at 85°C.

As the drying temperature was increased, the rate and amount of esterification increased. This is shown in Fig. 21. The rate of consumption of ASA also increased as the drying temperature was increased. This is shown in Fig. 22.

Drying Time

As the drying time was increased, the esterification reaction increased to a point and then stabilized. These results are shown in Fig. 21. At the 105°C drying temperature the ASA clearly continued to decrease after the esterification reaction appeared to cease, as may be observed in Fig. 23.

Because extraction of the samples with toluene decreases the acid level, the ASA hydrolysis product must be formed during drying. These results are seen in Fig. 24. Because the ester containing product would not be extractable, the hydrolysis product must be the extracted species and therefore is formed during drying.

Conditioning Time

The ester level could be observed to increase during conditioning in sheets that were extracted prior to examination. Unconditioned samples displayed noticeably lower ester levels than conditioned samples. This may be observed in Fig. 25. Sheet extraction with toluene was used to separate increases in the ester peak due to esterification, from apparent increases due to hydrolysis product formation. Extraction should remove the hydrolysis product, but not the ASA product bound to the cellulose as the ester. The ester increase was most noticeable in samples dried for short times, where there would be more residual ASA and a greater potential for change from unconditioned sheets.

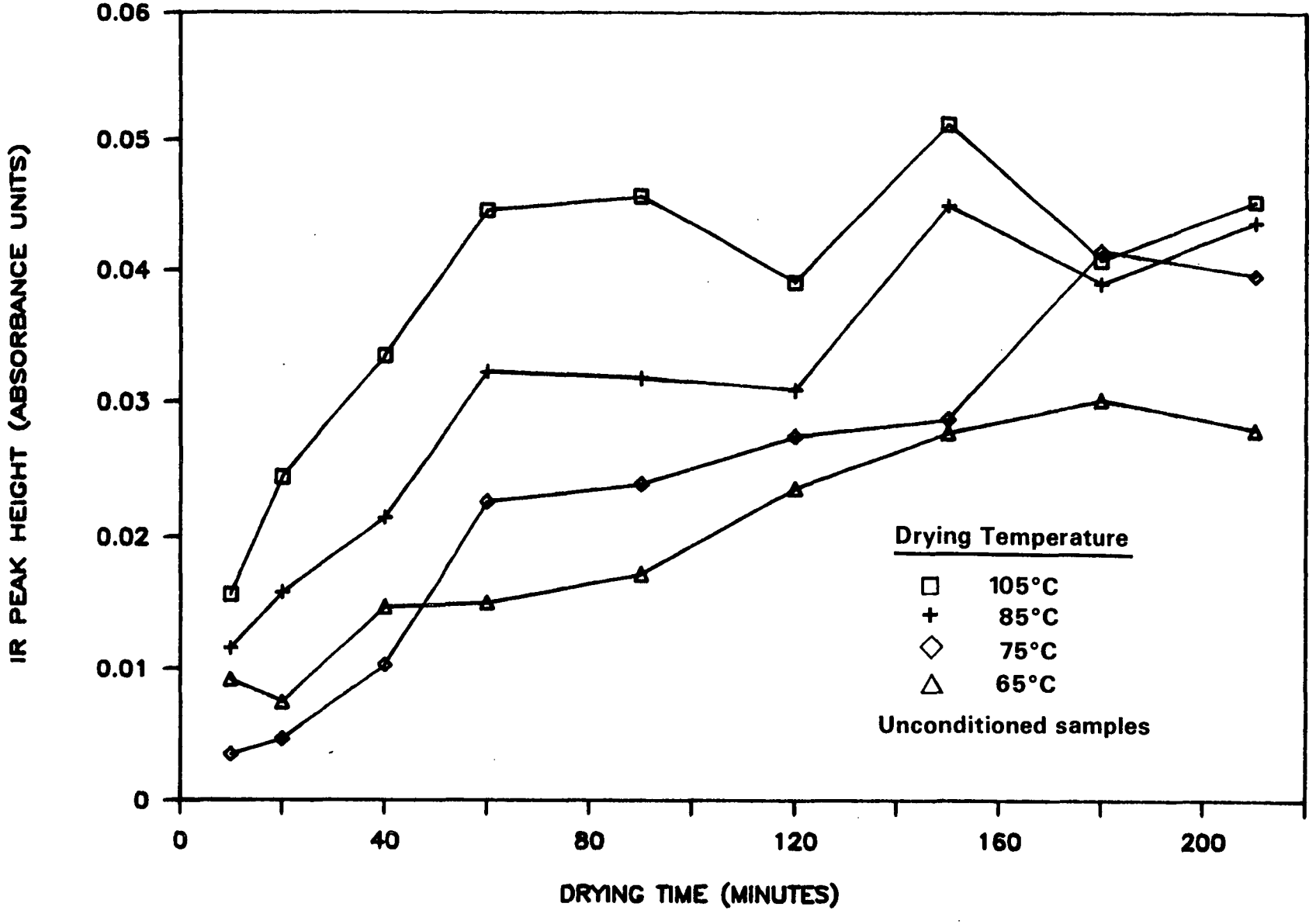


Figure 21. Subtractive DRIFTS results showing ester development during drying at ca. 1730 cm^{-1}.

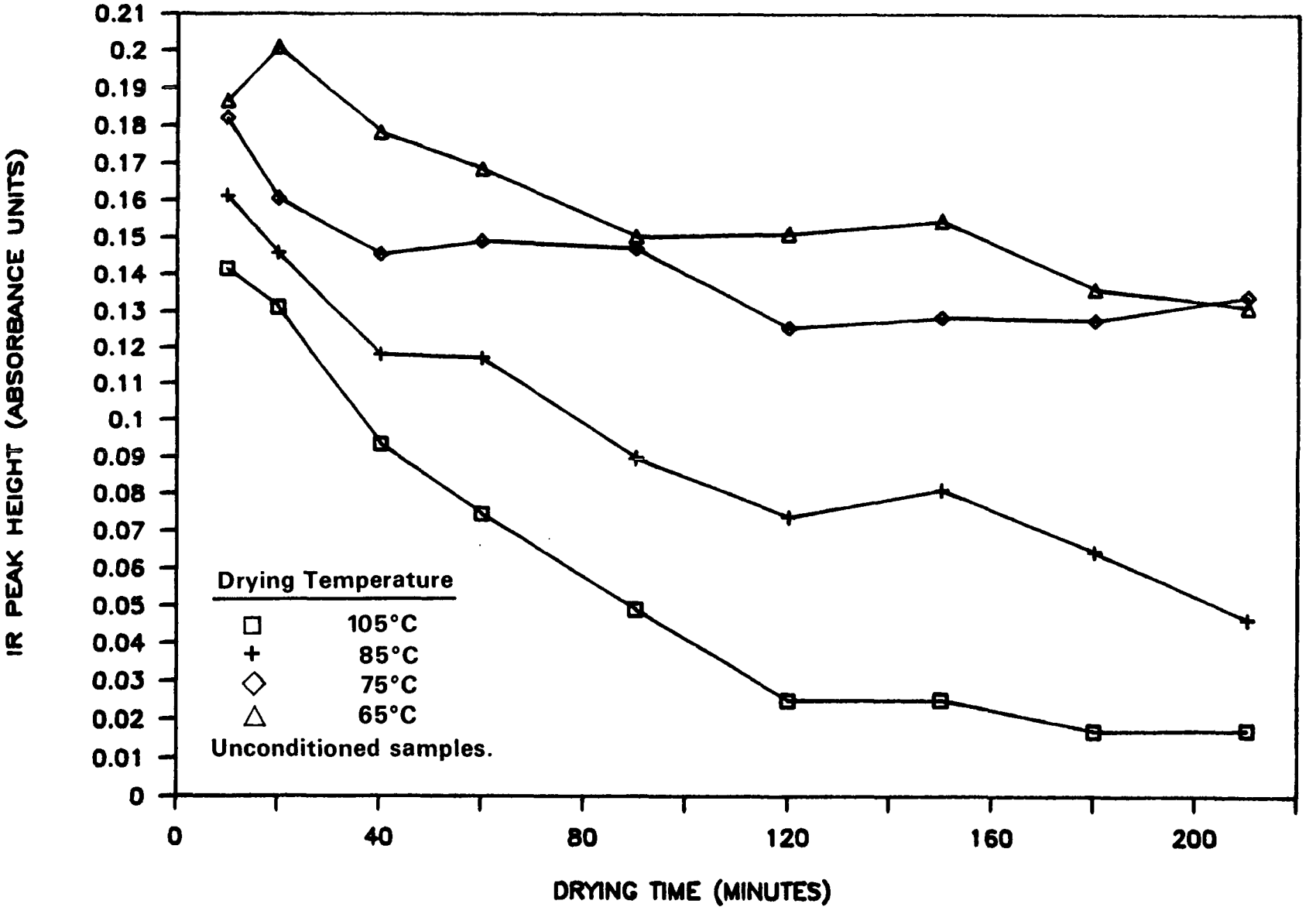


Figure 22. Subtractive DRIFTS results showing ASA consumption during drying at ca. 1785 cm^{-1}.

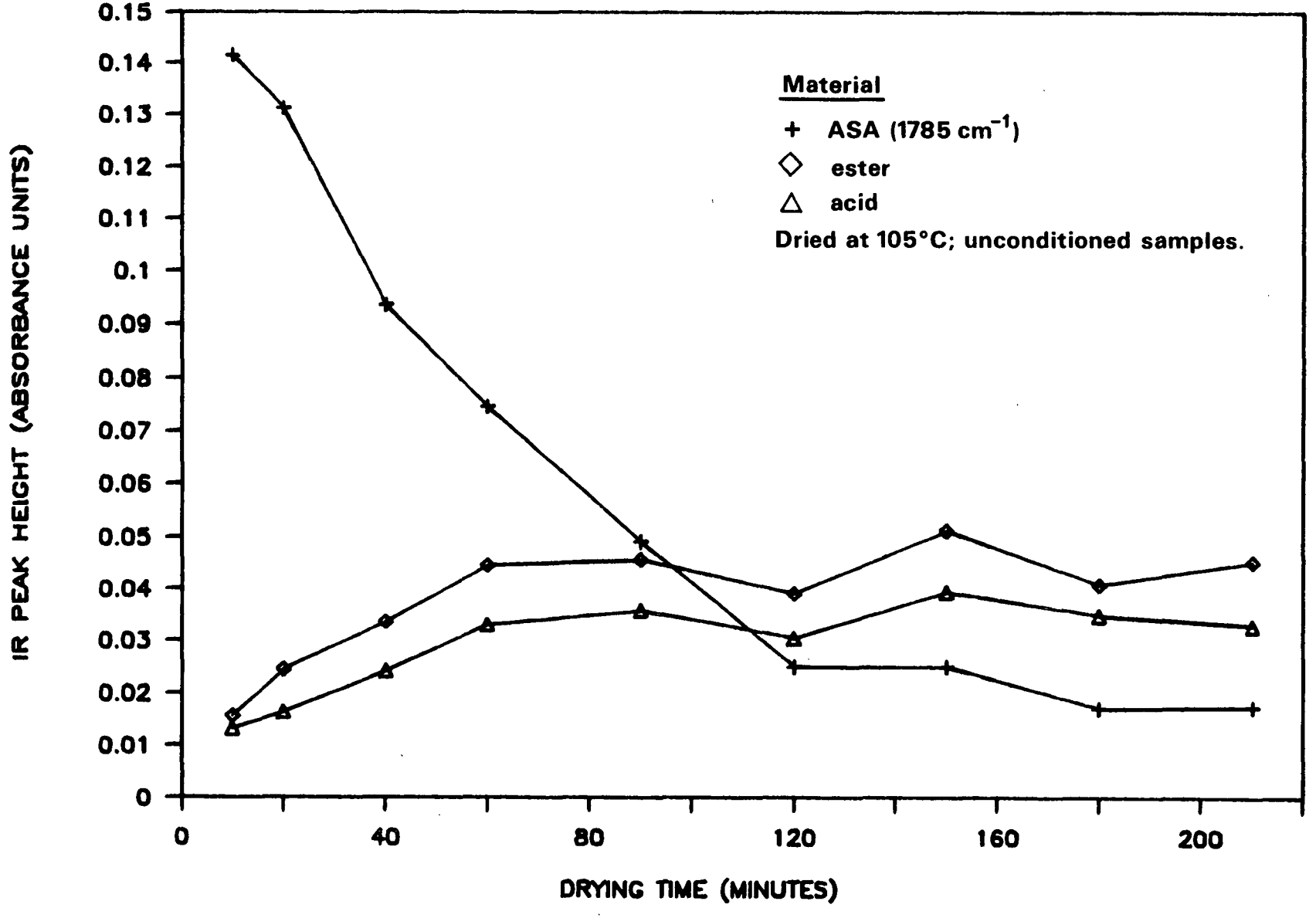


Figure 23. Subtractive DRIFTS results showing ASA consumption and ester and acid development (at ca. 1730 cm^{-1} and 1710 cm^{-1}, respectively), during drying.

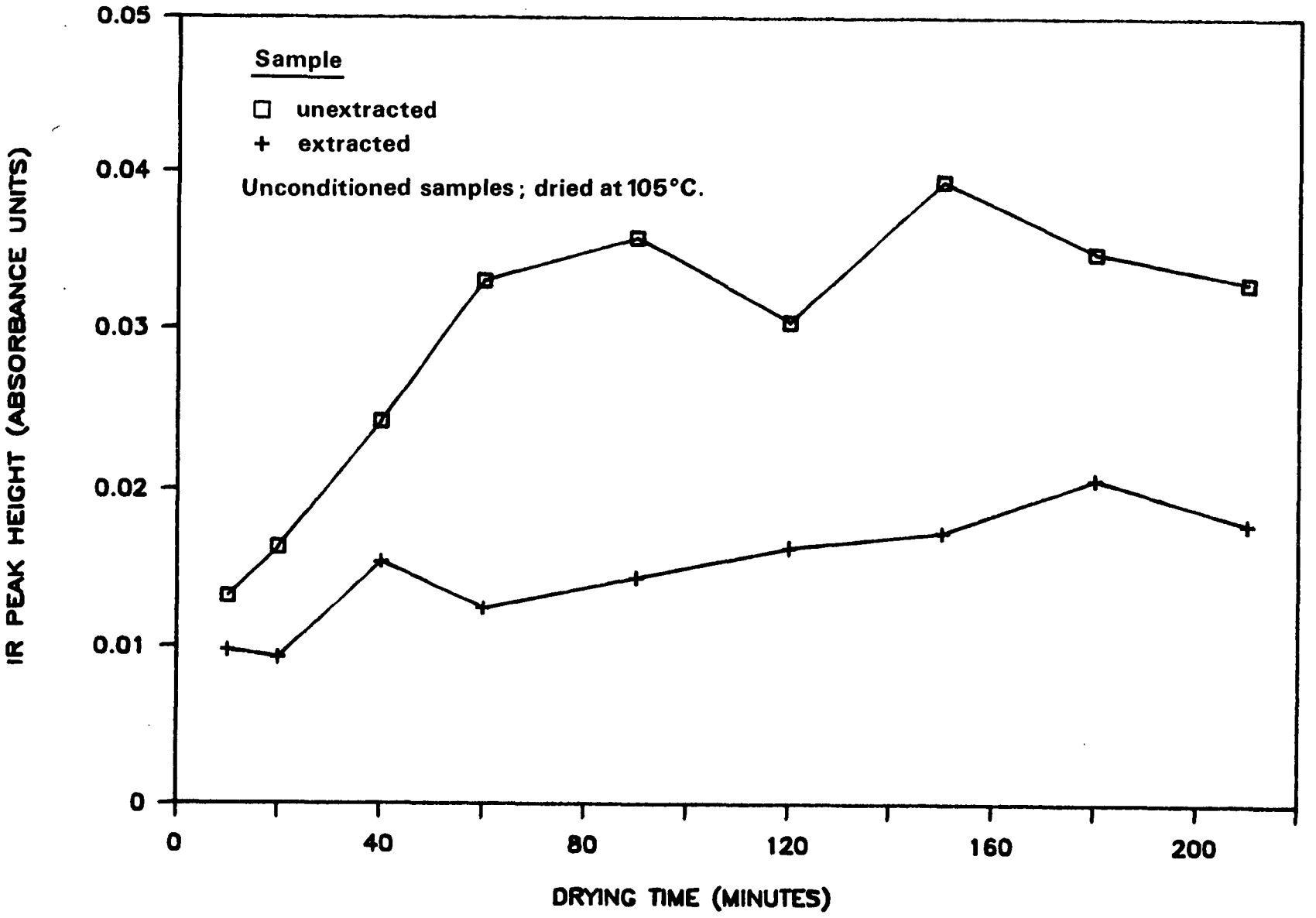


Figure 24. Subtractive DRIFTS results at ca. 1710 cm^{-1} showing acid loss from extraction. The samples were dried at 105°C.

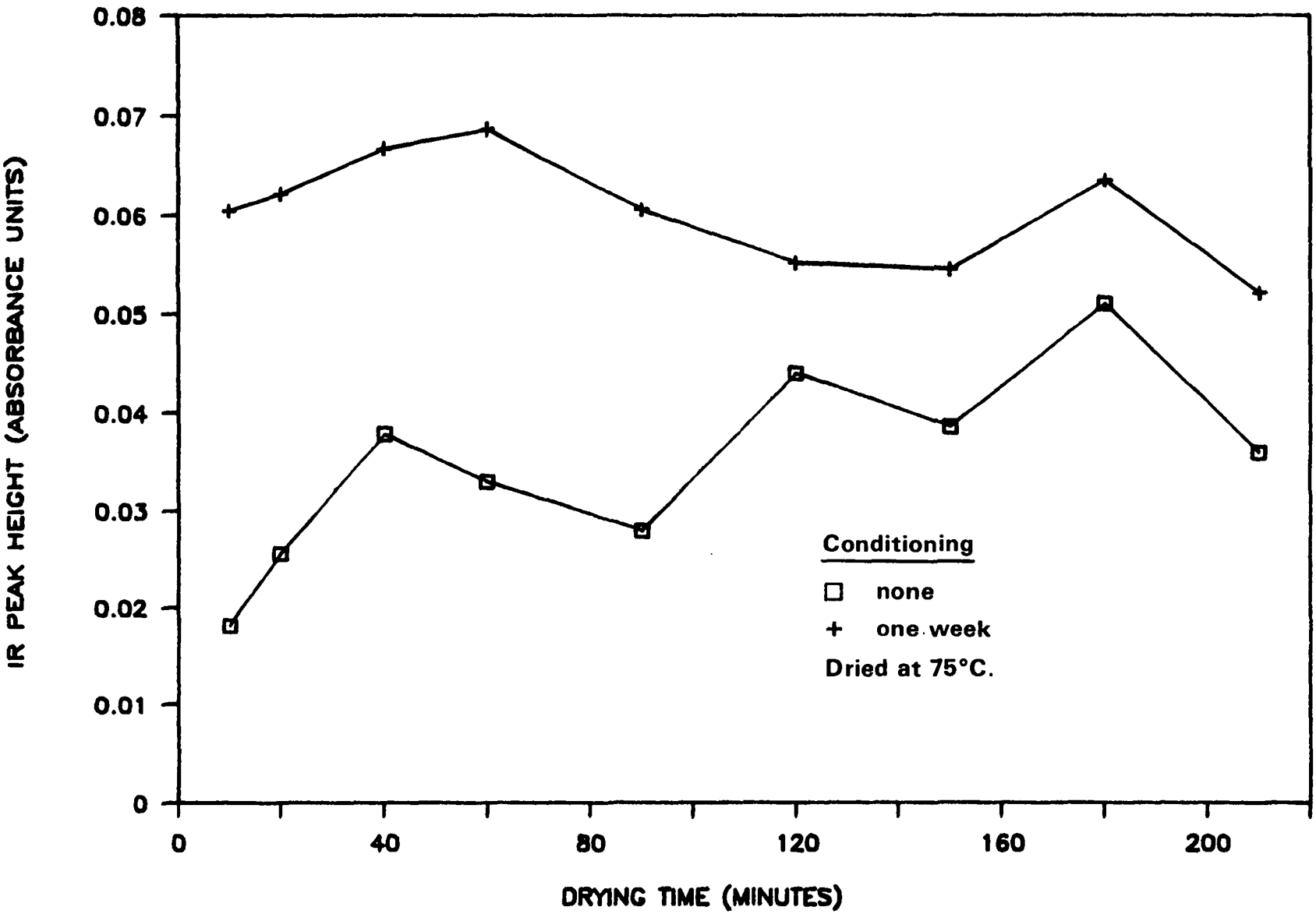


Figure 25. Subtractive DRIFTS results at ca. 1730 cm^{-1}, from sheets extracted after conditioning, showing ester development during conditioning.

Additionally, up to one day the acid level increased during a conditioning period of up to one day. This was displayed as an increase in the acid peak, as shown in Fig. 26. The acid increase could be judged to be largely due to hydrolysis of the residual ASA, since the ester level was greater than the acid level without conditioning the sheets, whereas with conditioning, the acid level noticeably exceeded the ester level. This is apparent in Fig. 27.

In conjunction with the ester and acid increases during conditioning, the ASA level could be observed to decrease, as shown in Fig. 28.

The acid peak was seen to decrease from the one day levels after one week of conditioning. This may be observed in Fig. 26.

It should be noted that sheets extracted with toluene several months after production still displayed evidence of the presence of ASA and the hydrolysis product in the extracts when examined by transmission IR spectrometry.

ASA MIGRATION EXAMINATION

Size Tests

In the third phase of this thesis three layered laminated sheets were used, and size tests of Layer 3 yielded evidence of sizing, as shown in Fig. 29. Size testing in this phase of the thesis was performed with an ink containing no formic acid and an 85% reflectance endpoint because the sizing levels were low. Sheets produced, dried, and tested similarly to Layer 3 but without being placed in the proximity of an ASA containing layer displayed no sizing. Sizing data from this phase of the thesis are presented in Appendix VIII.

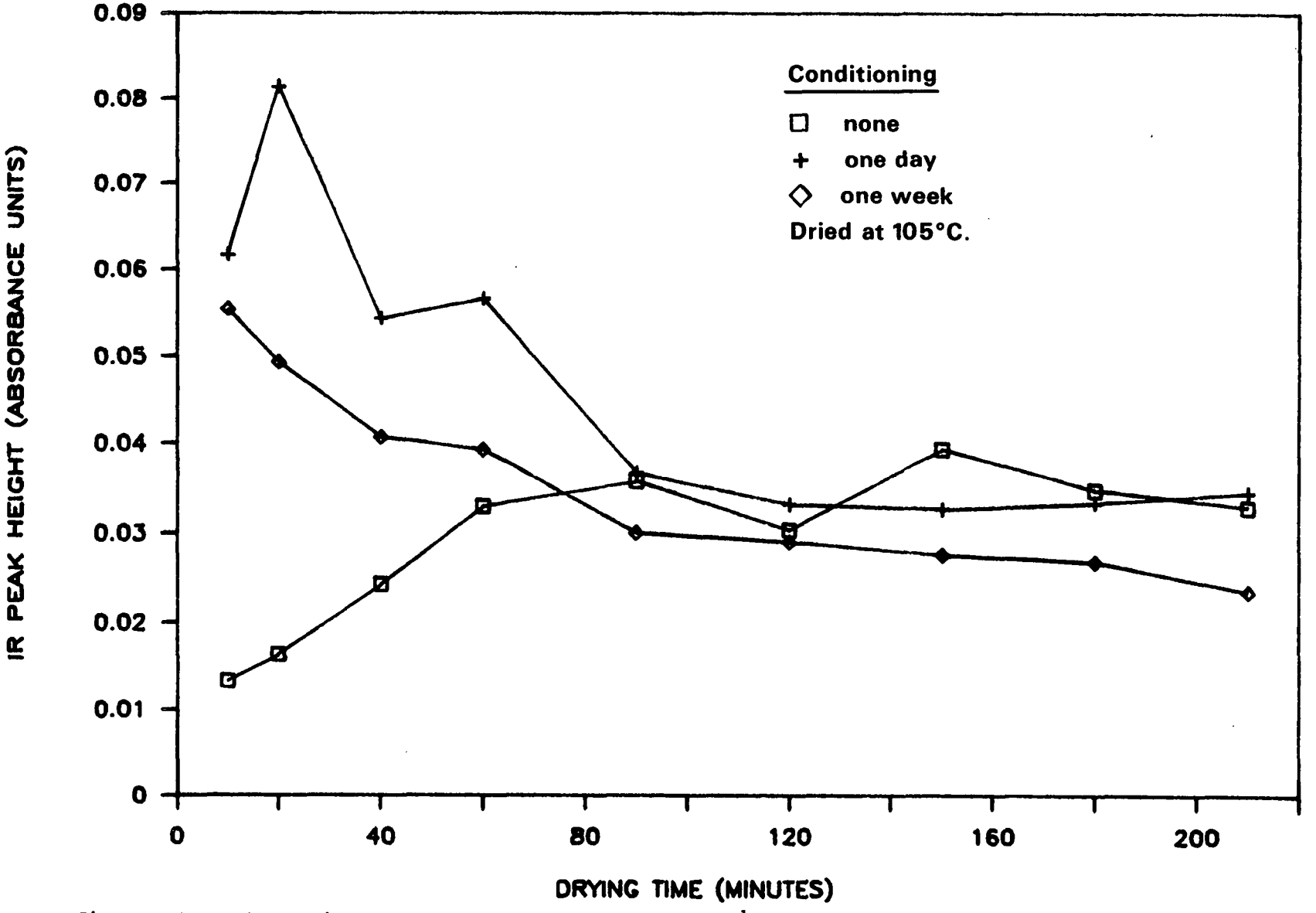


Figure 26. Subtractive DRIFTS results at ca. 1710 cm^{-1} showing acid development and loss during conditioning.

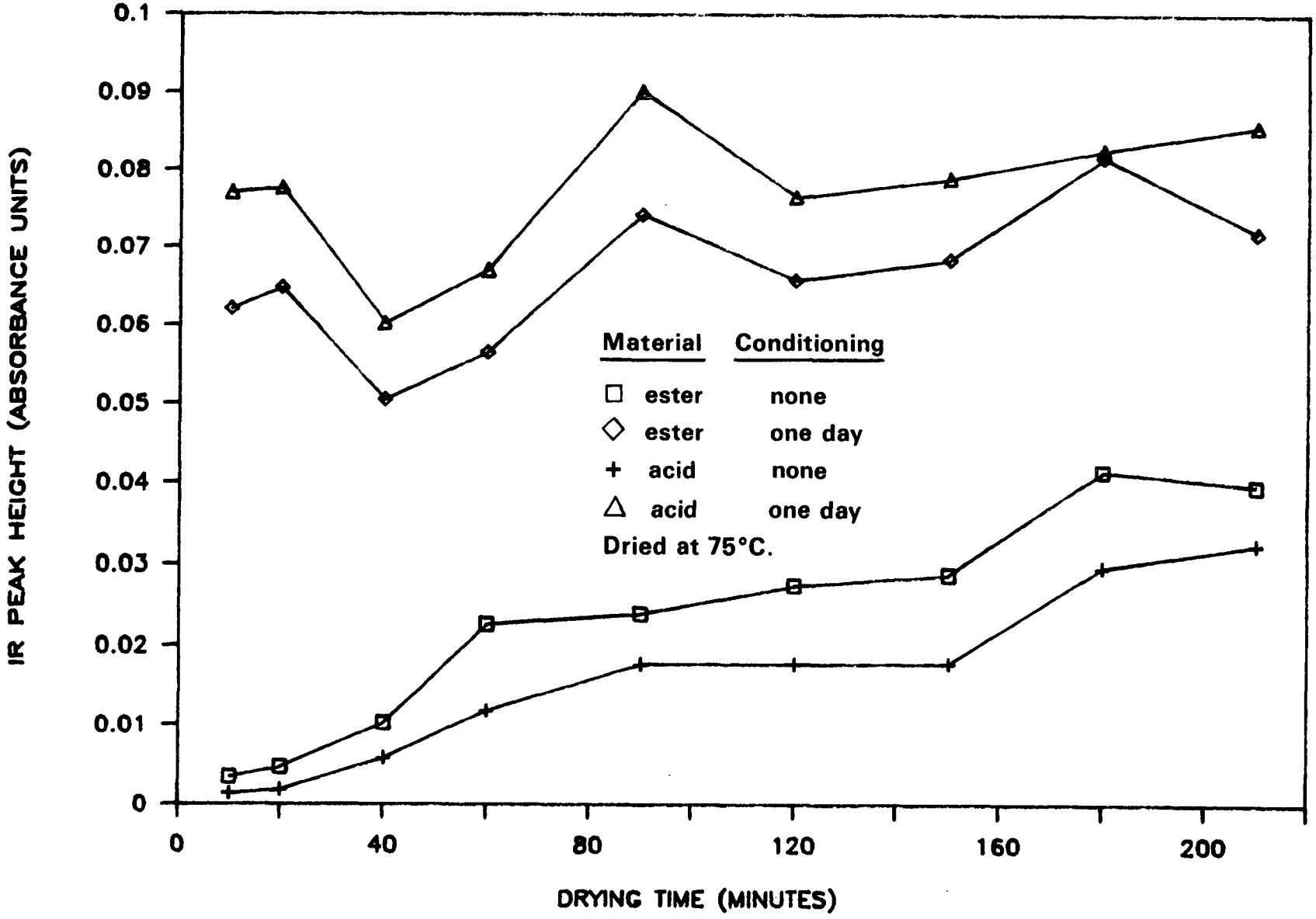


Figure 27. Subtractive DRIFTS results showing ester and acid development at ca. 1730 cm^{-1} and 1710 cm^{-1}, respectively.

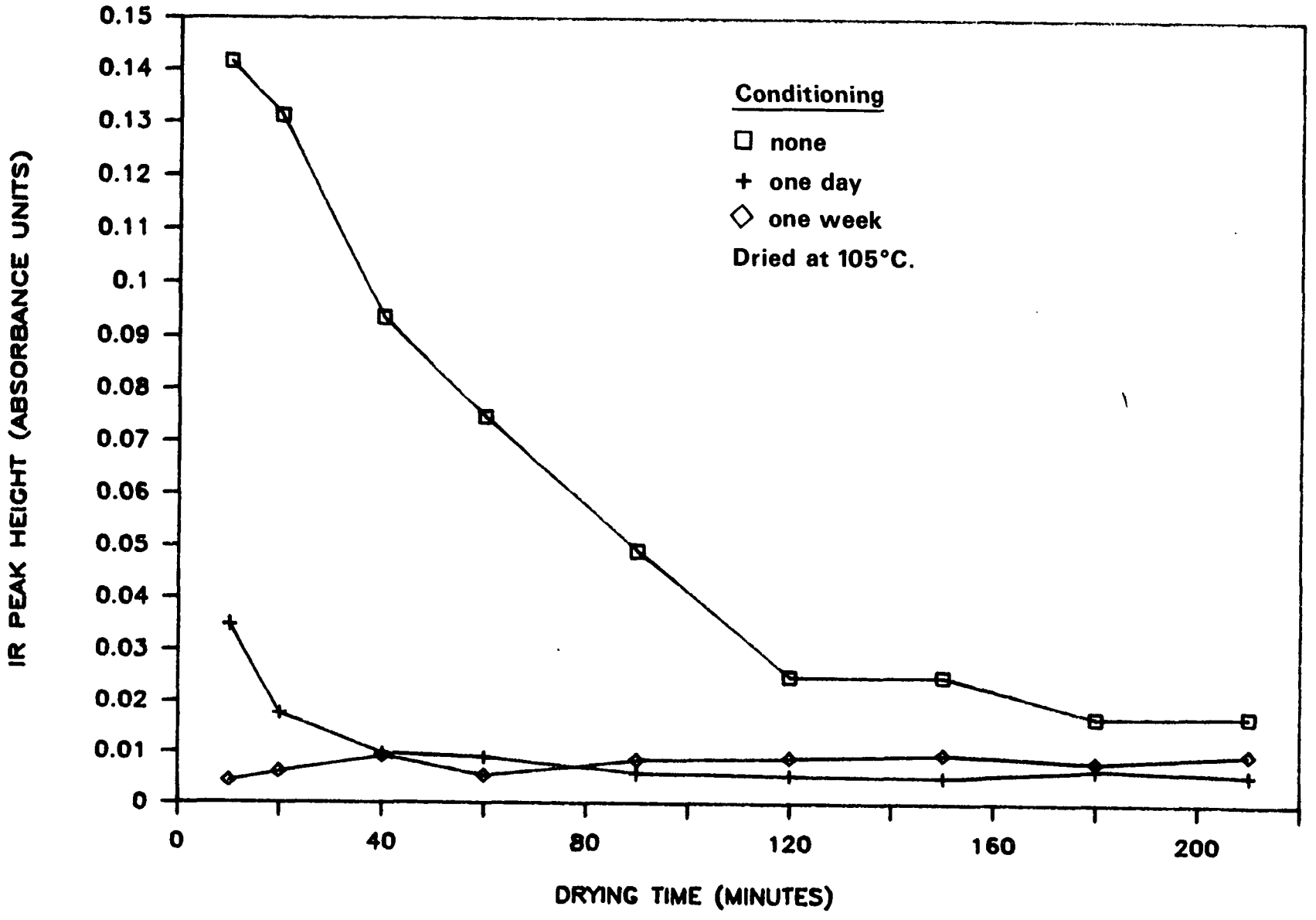


Figure 28. Subtractive DRIFTS results at ca. 1785 cm^{-1} showing ASA consumption during conditioning.

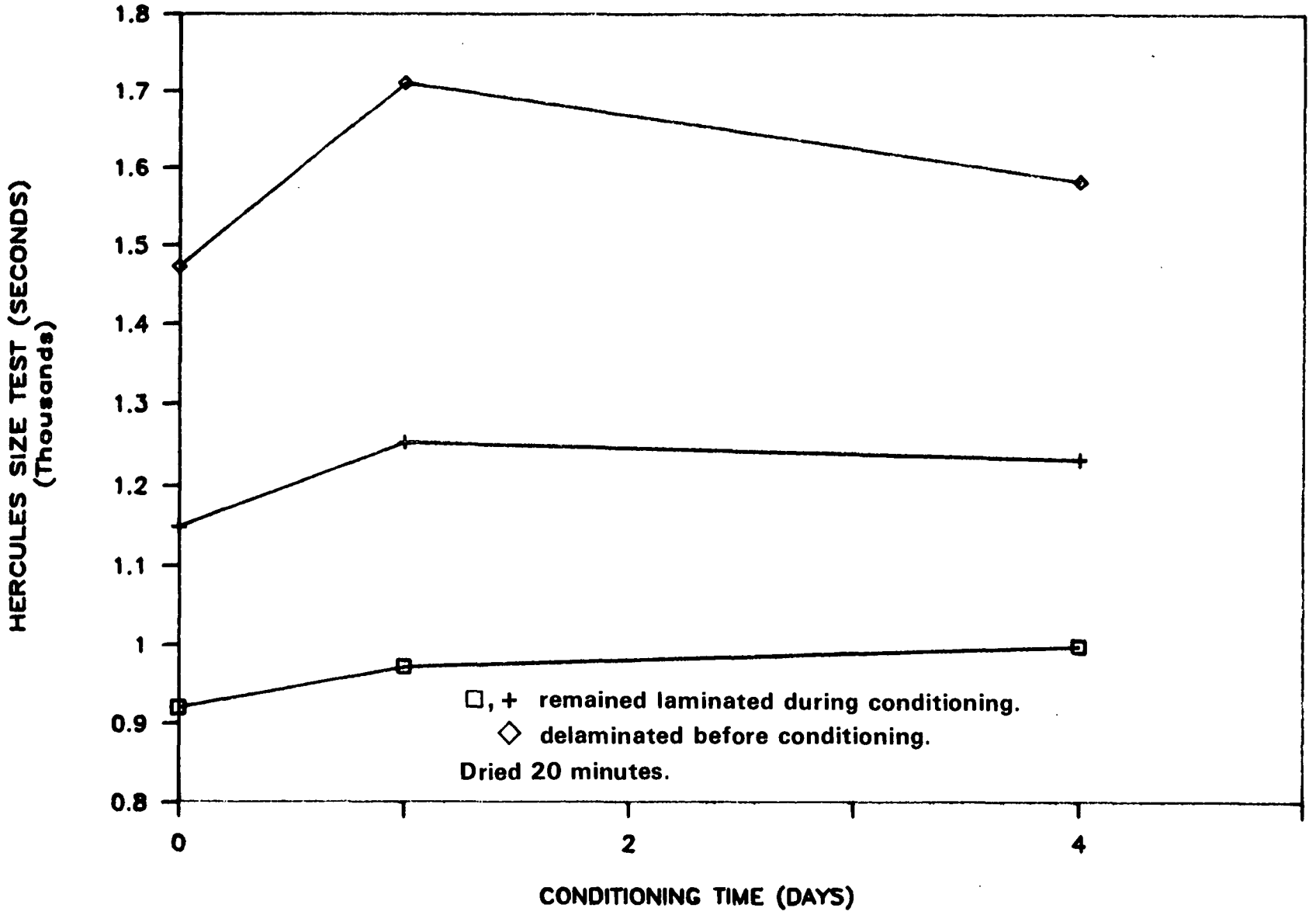


Figure 29. Hercules Size Tests of Layer 3 sheets with different conditioning levels.

In tests where Layer 3 remained laminated to Layers 1 and 2 during conditioning, sizing level increases were observed in conditioned samples after one day. The size tests remained stable after one day of conditioning. As may be seen in Fig. 30 the increase is more noticeable in sheets dried for 7 minutes. Where Layer 3 was separated from Layers 1 and 2 during conditioning, similar increases in sizing were evident in conditioned sheets. This is shown in Fig. 29.

All sizing data from the experimentation just described are included in Table 36 in Appendix VIII.

When Layer 1 contained only 0.15% ASA, no evidence was observed of sizing in Layer 3 after 20 minutes of drying.

It should be noted that even after 25 minutes of contact drying, Layer 1, containing 1.5% ASA, still displayed clear DRIFTS evidence of residual ASA. This is shown in Fig. 31. These results are also presented in Table 37 of Appendix IX.

Spectrometric Tests

In examining five layered sheets that were dried for 20 minutes, by DRIFTS, and their concentrated extracts by transmission IR spectrometry, clear evidence was seen for ASA migration during drying. By DRIFTS, in Fig. 32, ASA could be seen at ca. 1785 cm^{-1} in Layers 3 and 4 before conditioning. Further, the ester peak at ca. 1730 cm^{-1} and the acid peak at ca. 1710 cm^{-1} could be distinguished in Fig. 32. As shown in Fig. 33, by transmission IR spectrometry of the extract the ASA could also be seen at ca. 1785 cm^{-1} in Layer 5. All DRIFTS and transmission IR spectrometry evidence of ASA at ca. 1785 cm^{-1} decreased noticeably when sheets that were conditioned for one day, or one week, and extracts, were examined. This may be observed in Fig. 32 and 34, and more clearly in Fig. 35.

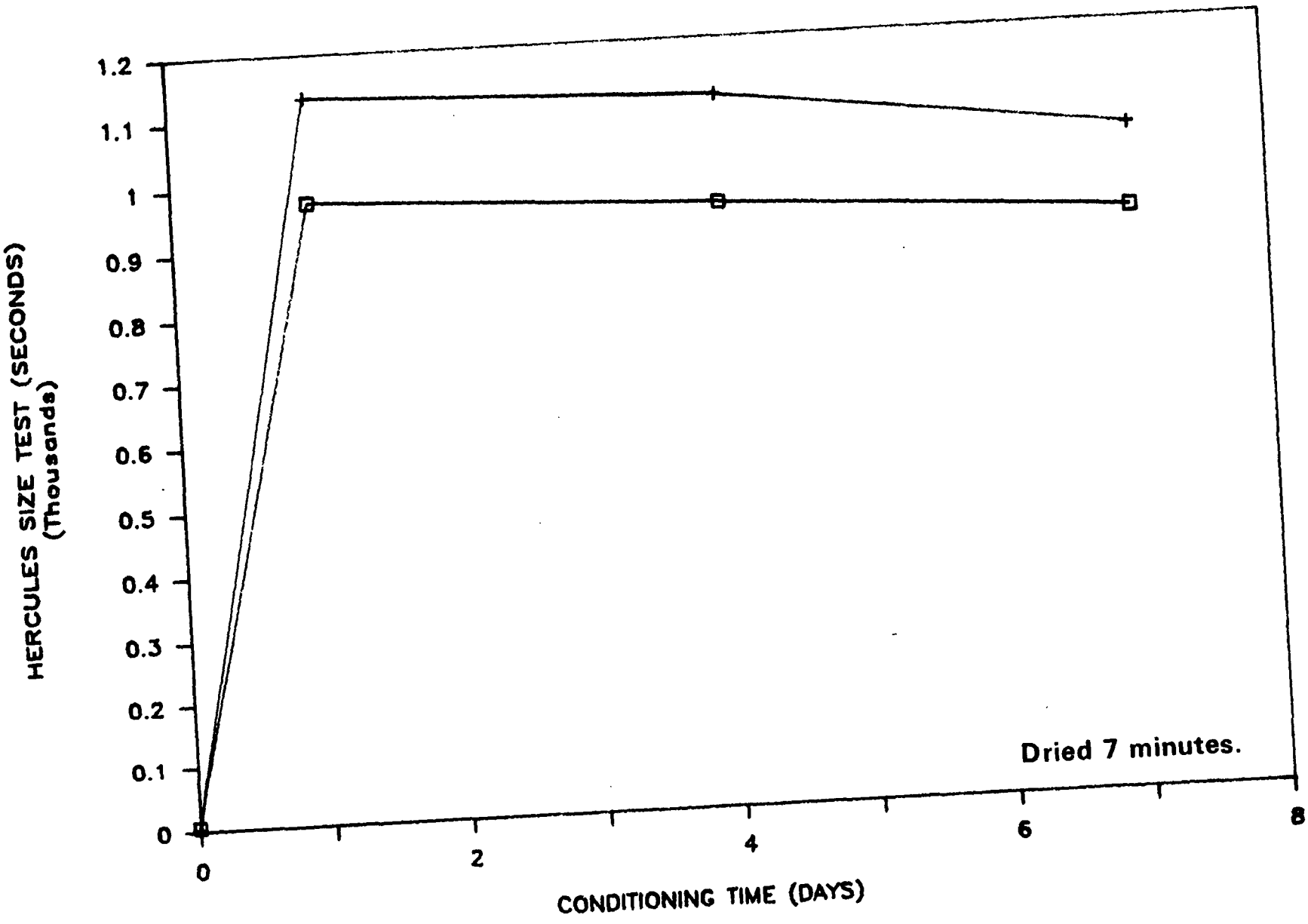


Figure 30. Hercules Size Tests of Layer 3 sheets with different conditioning levels. The two symbols indicate duplicate experiments.

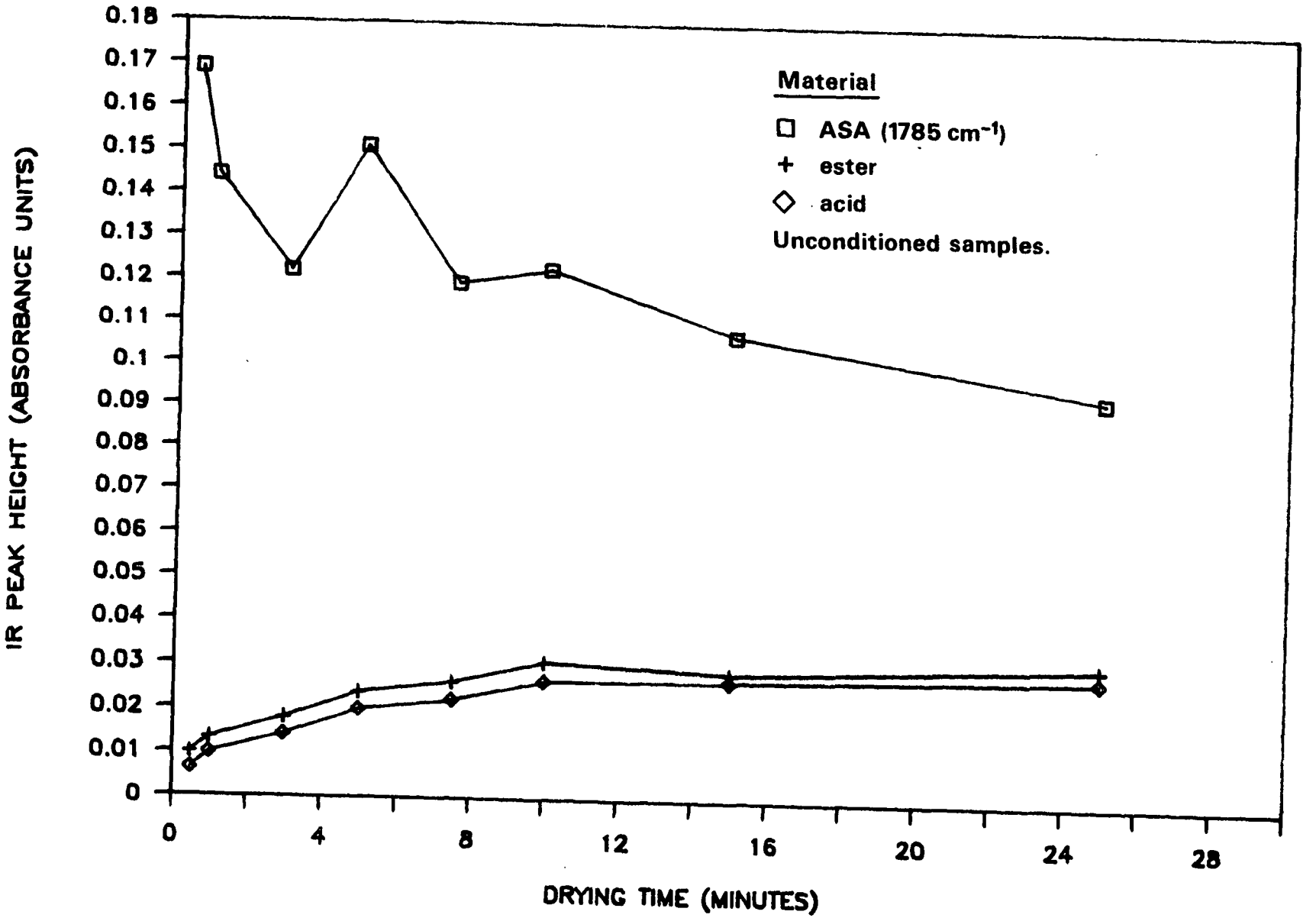


Figure 31. Subtractive DRIFTS results showing ASA, and ester and acid development (at ca. 1730 cm^{-1} and 1710 cm^{-1}, respectively), during drying.

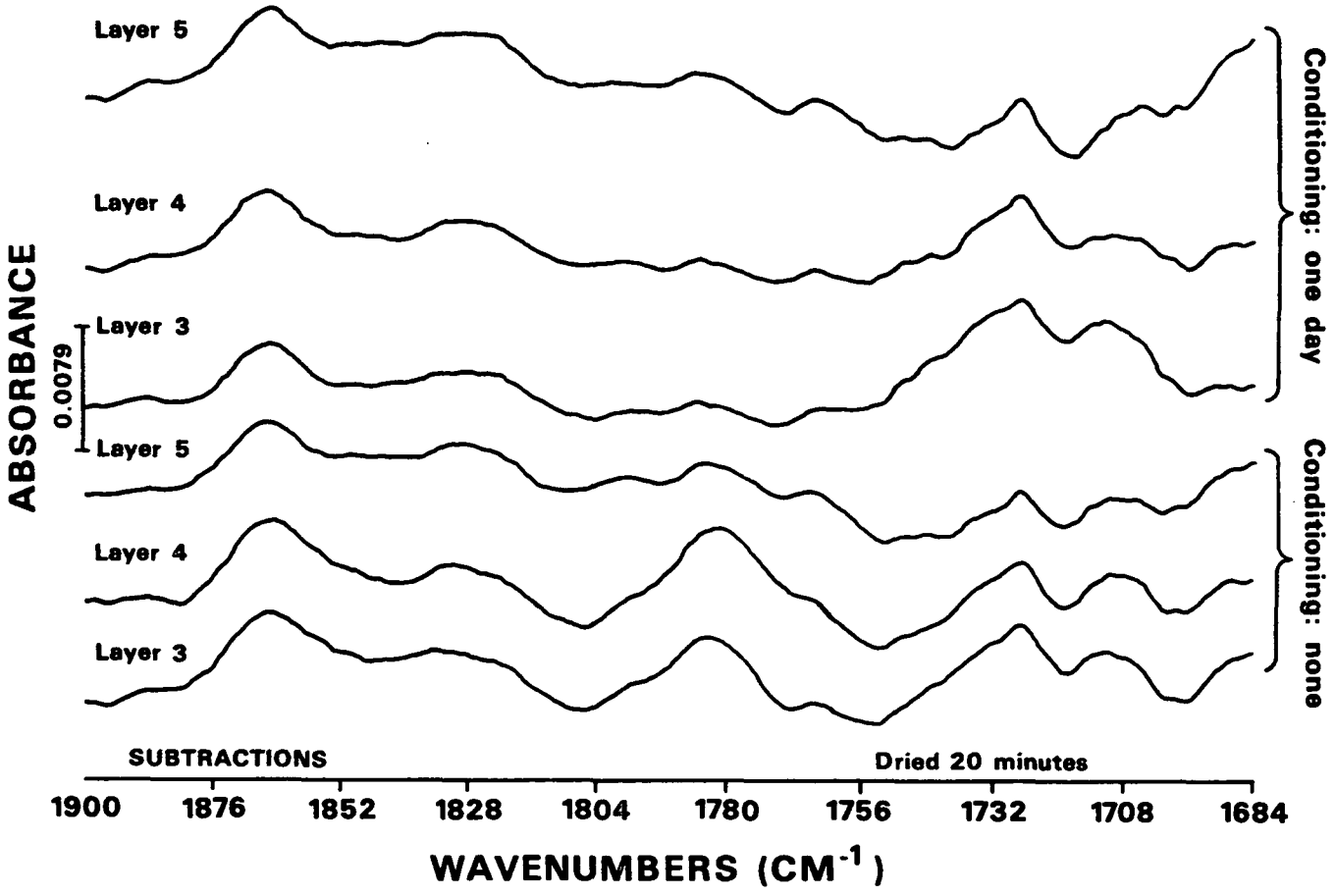


Figure 32. Subtractive DRIFTS results of Layers 3, 4, and 5 with and without conditioning.

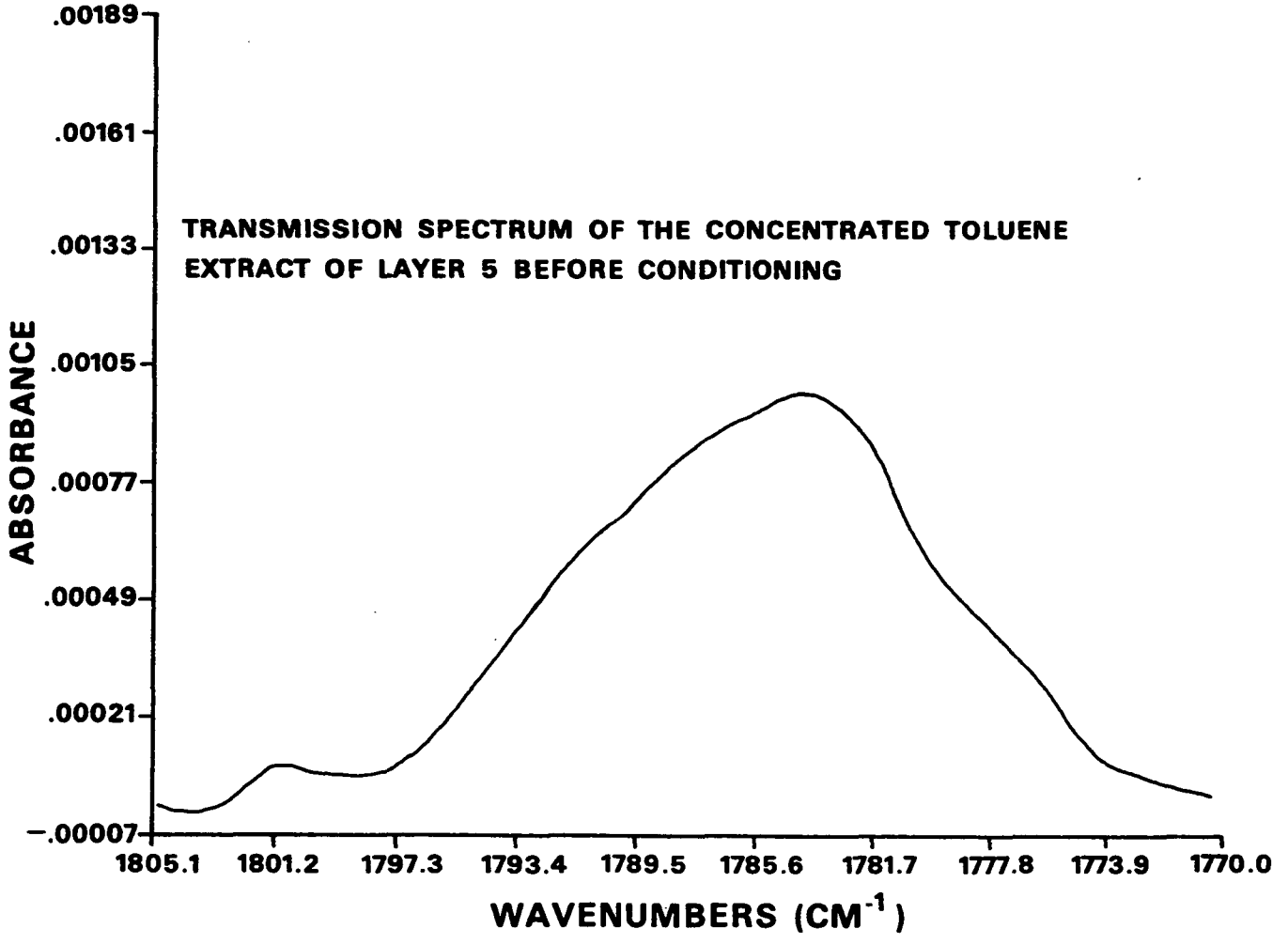


Figure 33. IR transmission spectrum of the concentrated toluene extract of Layer 5 immediately after drying.

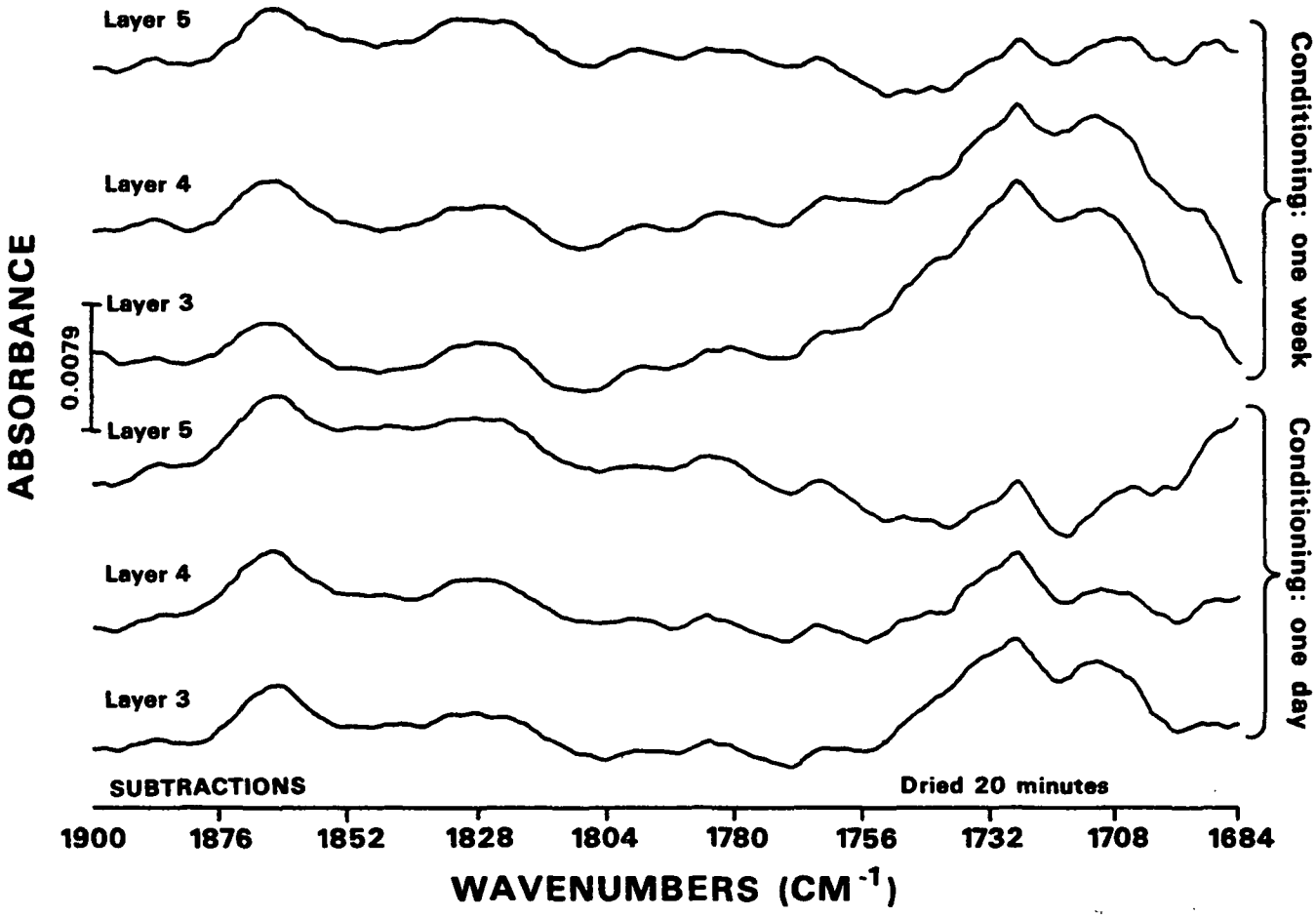
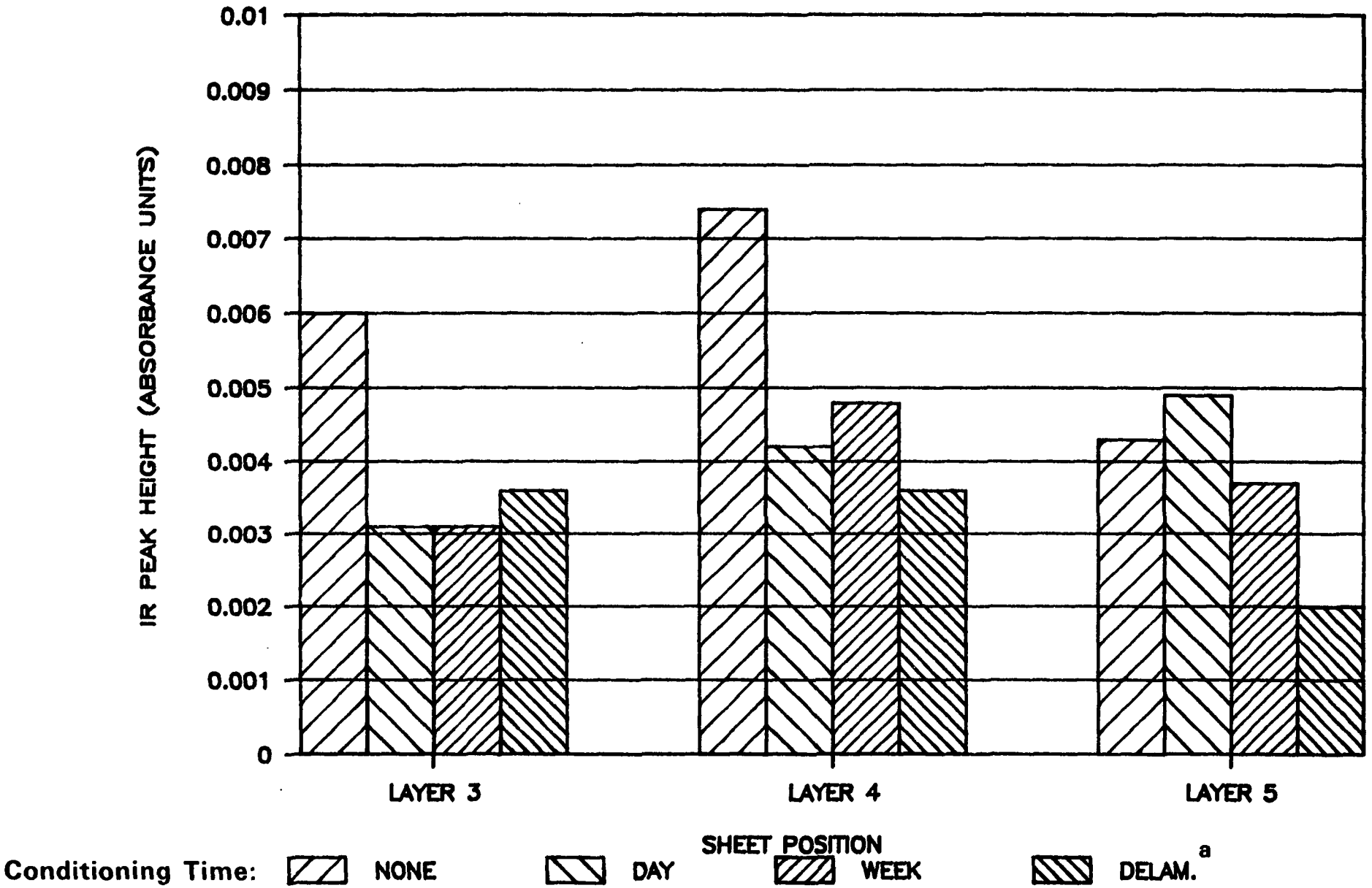


Figure 34. Subtractive DRIFTS results of Layers 3, 4, and 5 after conditioning.



[a] delaminated before conditioning one week.

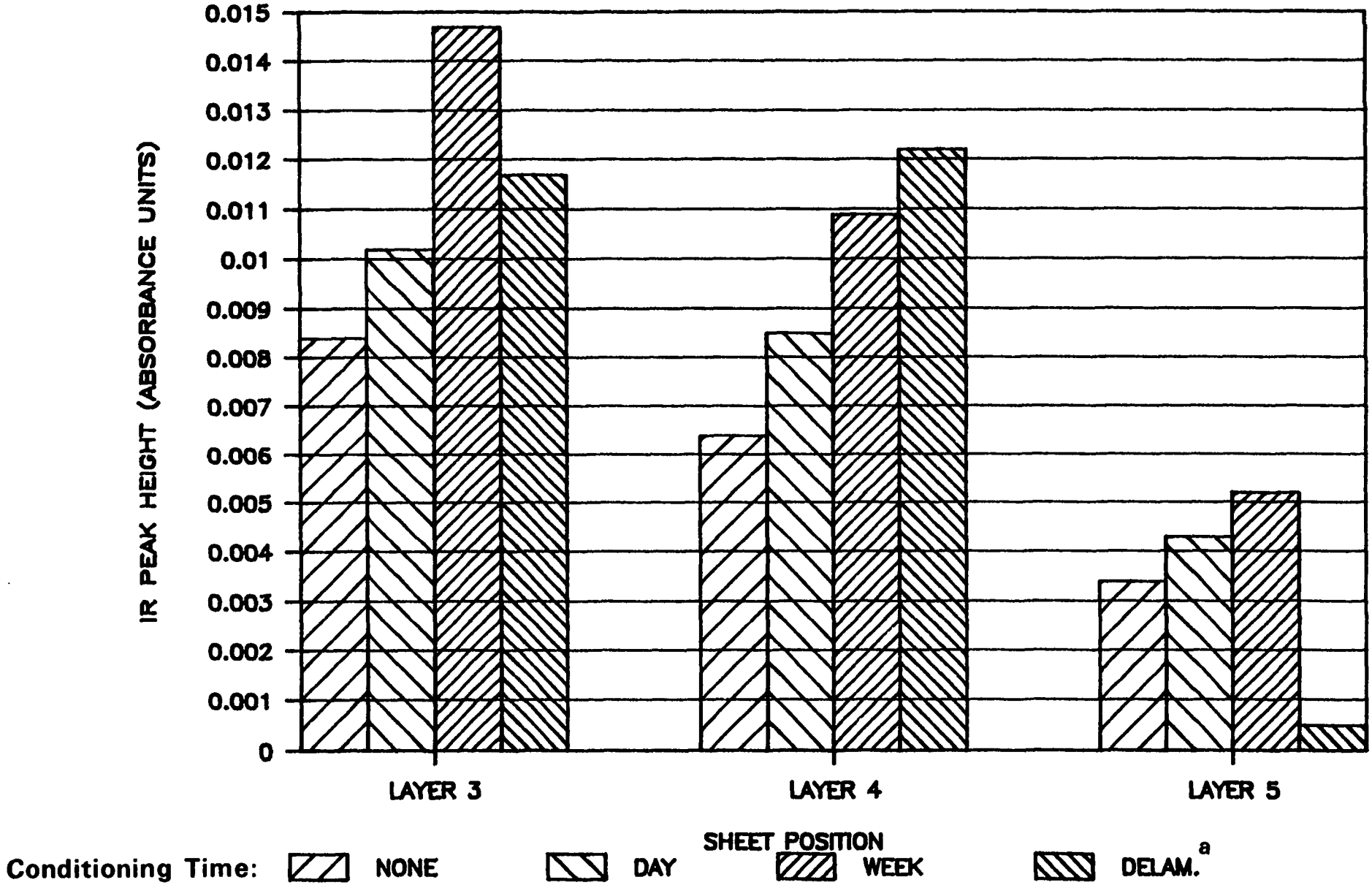
Figure 35. Subtractive DRIFTS results showing ASA levels and consumption during conditioning at ca. 1785 cm^{-1}.

It should be noted that DRIFTS examinations of Layer 5 were somewhat less accurate than those of Layer 3 and Layer 4, as the concentrations of the species of interest in Layer 5 were the lowest of Layers 3, 4 and 5.

With conditioning, clear evidence of further esterification was seen by DRIFTS at ca. 1730 cm^{-1}. The greatest ester level was seen in Layer 3. Layer 4 had a lower ester level, and Layer 5 had the lowest ester level. Similar trends were visible in examinations of the acid peak at ca. 1710 cm^{-1}, though the trends were less clear. The above results may be observed in Fig. 36 and 37.

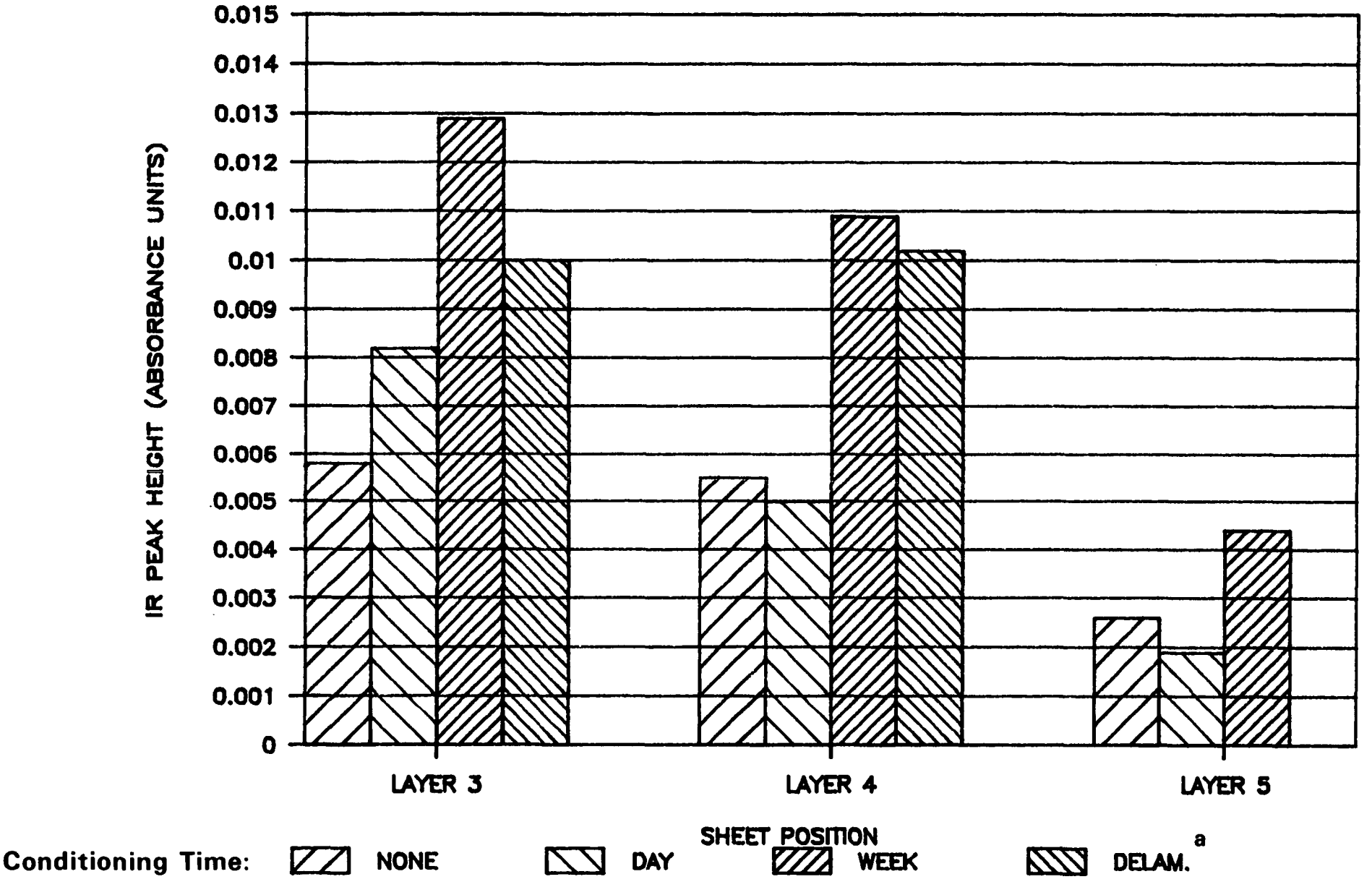
In comparing samples of the five layered sheets that remained laminated during conditioning and those that were separated before conditioning, no significant differences could be observed by DRIFTS in Layers 3 and 4, as shown in Fig. 36. The DRIFTS data observed for Layer 5 are questionable, since, as noted previously, the concentrations of species are relatively low in Layer 5.

All IR data from five layered sheets are presented in Appendix IX in Table 38.



[a] delaminated before conditioning one week.

Figure 36. Subtractive DRIFTS results showing ester levels and development during conditioning at ca. 1730 cm^{-1}.



[a] delaminated before conditioning one week.

Figure 37. Subtractive DRIFTS results showing acid levels and development during conditioning at ca. 1710 cm^{-1}.

DISCUSSION

EVIDENCE OF ESTERIFICATION

The reaction of ASA with cotton linters in N,N-dimethylformamide established that the substituted succinic anhydride can react to form an ester with the cellulosic substrate used in this work. Further, it established clearly the ester peak position and shape, as shown in Fig. 14. The latter aspect was important because the acid peak (ca. 1710 cm^{-1}) is adjacent to the ester peak (ca. 1730 cm^{-1}). Knowledge of what to look for, for ester evidence in a papermaking system, was necessary. Additionally, locating the position of the ester in the IR spectrum was important, since knowing where to examine the DRIFTS spectra of handsheets was as necessary as knowing what to look for. This is particularly true, since the position of the ester was somewhat lower in frequency than anticipated. Reaction of the ASA with ethanol had produced an ethyl ester IR peak at ca. 1739 cm^{-1} as shown in Fig. 38. Additionally, a peak at ca. 1710 cm^{-1} appeared as a result of carboxylic acid formation in conjunction with ethanol-ASA esterification. It was expected that an esterification reaction of ASA with cellulose would produce an IR peak at approximately the position noted above (i.e., 1739 cm^{-1}), though it was realized that using different reactants could cause a shift in the IR ester peak.

The position of the ASA-cellulose ester peak observed in this thesis is in close agreement with that found by Cuculo and Bowman.[57] Using reactants similar to, but not precisely the same as those used in this thesis, they found an ester peak at 1730 cm^{-1}.

Determining that ASA may react covalently with cellulose to form esters in a papermaking system, as shown in Fig. 15, was important to this work, since it

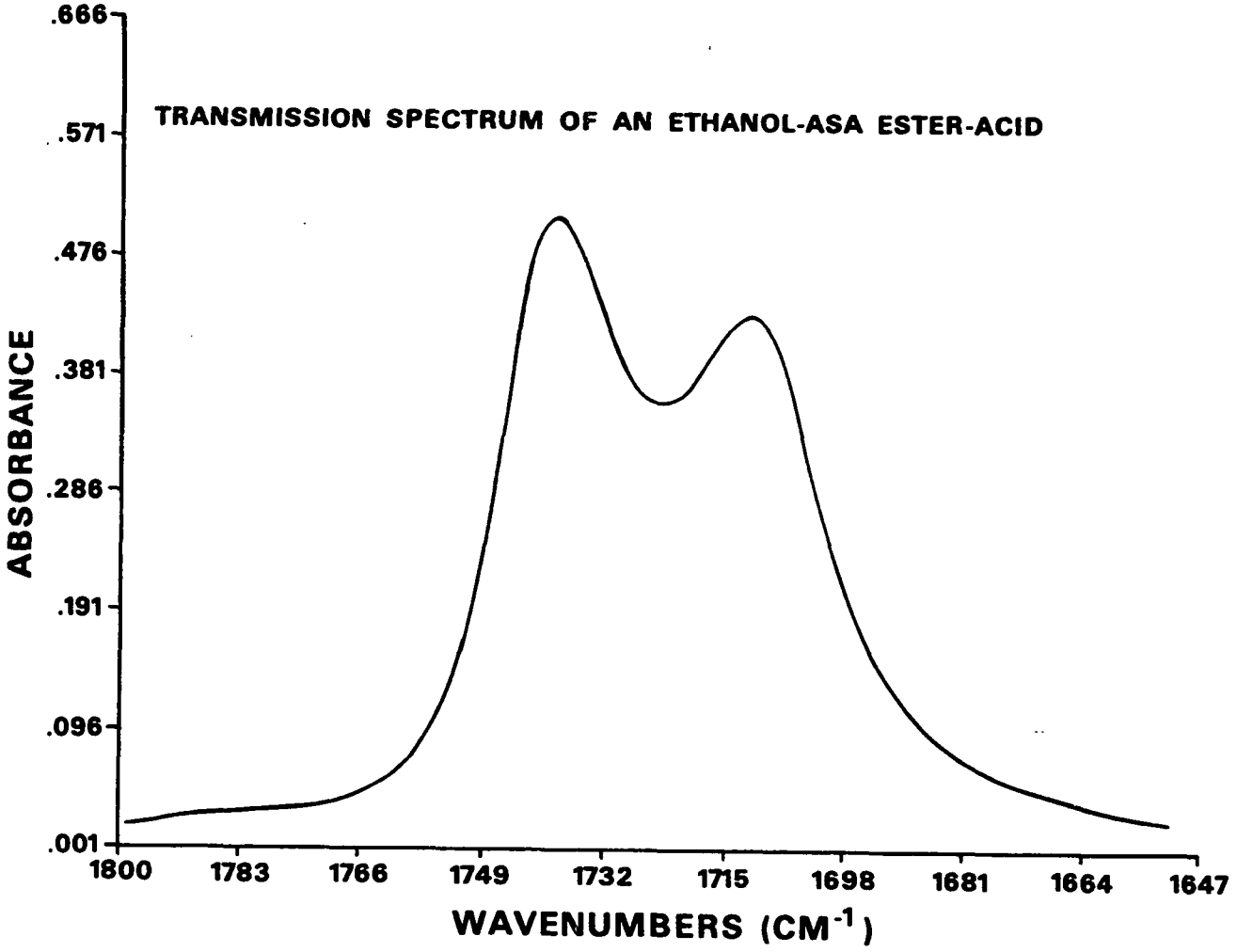


Figure 38. IR transmission spectrum of an ethanol-ASA ester-acid.

completed one of the objectives of this thesis, provided a clear direction in which to proceed with the other objectives and established an experimental chemical system and procedure for future work.

THE HYDROLYSIS PRODUCT AS A SIZING AGENT

The hydrolysis product of ASA was reasonably ruled out as a significant sizing agent in the system examined, using the results of Table 1 and size tests of the sheets described in Appendix IV. It must be assumed that the conditions and chemical species encountered by the hydrolysis product in this system when the ASA hydrolyzed, were also encountered when the ASA hydrolysis product was added to the system by itself. Since no sizing was encountered in the latter case, the ester must be the product that promotes sizing in this system. This idea could reasonably be extended to commercial systems. Further, sheets with delayed pressing and drying should promote hydrolysis and yield reduced sizing relative to sheets pressed and dried immediately after formation. Since reduced sizing was observed in sheets with delayed pressing and drying in Table 1, this is additional evidence for the hydrolysis product being a nonsizing agent (i.e., inactive as a sizing agent).

The above conclusion that the ASA hydrolysis product is an inactive sizing agent is compatible with Wasser's[43] results. Wasser reported the hydrolysis product to be a desizing agent (i.e., a wetting agent), but no attempts were made in this thesis to determine whether the hydrolysis product was a desizing agent in addition to being a nonsizing agent.

The rapid consumption of ASA as shown in Fig. 23-26 and Fig. 28 as either the hydrolysis product or the ester, and also its elimination through volatilization which will be discussed later, would indicate that the unreacted

ASA cannot provide stable sizing by itself. The ASA is rapidly eliminated from the environment of the sheet to a great degree.

EFFECTS OF EMULSION AGING AND SHEET MOISTURE

In the case where pressing and drying of an ASA containing sheet was delayed (see Table 1), promotion of the ASA hydrolysis product in preference to the ester must be expected. Farley[58] has stated that the material doctored off press rolls in an ASA system is enriched in hydrolyzed size. Since the doctored material would have significant contact with moisture, it is reasonable to anticipate that sheets produced with delayed pressing and drying should have had ASA hydrolysis promoted, as the ASA also had significant contact with moisture under those conditions. The fact that sizing was significantly decreased under these conditions provides additional evidence that the ester must promote sizing, at the least to a much greater extent than the ASA hydrolysis product can.

In examining the effect of emulsion age and aging of the sheet before pressing and drying, the sizing results in Table 2 may be explained by the detrimental effects of both aging processes. An older emulsion leads to ASA hydrolysis and resultant lower sizing. An older sheet allows more time for ASA hydrolysis to occur in the sheet. The fact that the last sheet made has the highest sizing can be interpreted as meaning that hydrolysis of ASA in the sheet is more harmful to sizing than hydrolysis of ASA in the emulsion. The decrease and subsequent increase in sizing can be interpreted as the trend resulting from the additive detrimental effects of aging the emulsion and the sheet.

SIZING AS A FUNCTION OF DRYING

Drying Temperature

Results showing more rapid sizing development with an increased drying temperature, as seen in Fig. 16, are reasonable to expect in a sizing system reliant on covalent reaction for a mechanism. As the drying temperature increases, the esterification reaction should be accelerated and sizing should develop more rapidly. These results agree with those of Wasser's[43] in which sheets were sized with ASA in toluene, and with Poppel's and Bobu's[33] in which AKD was used.

The superior sizing test maxima seen at higher drying temperatures in Fig. 16 could be related to the balance of products achieved at different temperatures. At higher drying temperatures moisture would be eliminated from the sheet more quickly and completely, yielding less opportunity for the hydrolysis product to form. Logically, this provides a better chance for the ester to form and sizing would be expected to be superior where the ester was in greater abundance.

Drying Time

The effect of drying time observed in Fig. 16 can also be logically explained in terms of covalent reaction. As the drying time increases, the esterification reaction should become more complete. In a sizing system functioning through a covalent linkage, this could only result in an increased sizing level. Poppel and Bobu[33] also reported increases in sizing of AKD sized sheets with an increasing drying time.

The decrease in sizing at long drying times, as shown in Fig. 16, was unexpected. The source of the decrease may be formation of the hydrolysis product

in the absence of esterification at long drying times. Absence of esterification at long drying times could be explained by the consumption of all potential cellulosic esterification sites. If the assumption were made that the ASA hydrolysis product is a desizing agent, as has been suggested by Wasser,[43] then this explanation could be possible. Formation of the hydrolysis product after a long term of drying is difficult to accept, since water is clearly essential to hydrolysis, and drying would remove it. If a very small amount of hydrolysis could yield considerable desizing, or if only a very small quantity of water was required for hydrolysis, then the hypothesis suggested would be possible. It should be noted that based on an ASA addition rate of 0.15% and an ASA molecular weight of 322 grams per mole (see Appendix III), and assuming 100% ASA retention and 100% ASA hydrolysis, only 0.0084% water would be required for the hydrolysis. Thus, only a very small quantity of water is actually necessary.

Conditioning Time

The effects of conditioning of less dried sheets on sizing seen in Fig. 17 are completely in keeping with the ideas expressed above. At short drying times the ASA would be less completely converted to either the hydrolysis product or the ester, when compared with longer drying times. Thus, the ASA is available for further reaction after drying (i.e., during conditioning) and yields additional sizing through esterification when compared with sheets tested immediately after drying. Strazdins[59] reported results in which sheets sized with ASA in a solvent displayed increases in sizing during conditioning. Additionally, Dumas and Evans[40] reported increases in sizing after conditioning for sheets sized with AKD. Though this thesis concerns ASA, the parallel between Dumas' and Evan's conditioning work and the work in this thesis is

completely reasonable to expect once the assumption is made that both the AKD and the ASA systems function through a covalent mechanism.

Since the hydrolysis product might be expected to form to a greater degree during conditioning than the ester because of the greater availability of atmospheric moisture compared to during drying, it is expected that the sizing level would not have the potential to exceed the maxima seen in unconditioned sheets. As may be seen in Appendix V in Tables 5-8, this is only true at 85 and 105°C, where it might be concluded that esterification was completed sometime during the 180 minute drying period. By completion of esterification it is meant that all potential cellulosic esterification sites have been consumed, even though some unreacted ASA may remain. At 65 and 75°C it might be concluded esterification was incomplete even after 180 minutes of drying, and that further esterification could occur during conditioning that could lead to sizing and esterification levels exceeding those seen in unconditioned sheets.

Type of Drying

The reason for the difference in sizing results observed between oven and contact dried sheets in Fig. 19 is not readily explainable with the data obtained in this thesis. It is possible that the difference is related to a difference in size distribution during drying, volatilization of a species, or a change in the amounts of the species obtained. This is purely conjecture, however.

REACTION AS A FUNCTION OF DRYING

Drying Temperature

The increase in esterification rate and amount seen with an increased drying temperature in Fig. 21 is quite reasonable. Generally, an increased

temperature yields a higher reaction rate constant.[60] Lindstrom[35] observed that the AKD reaction rate increased as the drying temperature increased.

An increase in the esterification rate with increased temperature would have to be related to an increase in the ASA consumption rate, as shown in Fig. 22; as products are formed more rapidly, reactants must be consumed more rapidly.

Drying Time

The eventual stabilization of the ester level seen in Fig. 21 is to be expected. After a certain time of reaction, it is likely that a significant portion of the potential cellulose reaction sites have been filled; then the reaction must slow down as reaction sites become more difficult to obtain access to. Additional esterification must involve diffusion of the ASA, beyond any initial diffusion, to reaction sites that have not been consumed.

The continued decrease in ASA level after the ester has stabilized, as seen in Fig. 23, can easily be explained by volatilization of the ASA.

Formation of the ASA hydrolysis product during drying, as suggested by the results seen in Fig. 24, is a result of the high reactivity of the ASA functional group. While drying would remove water from the sheet, there is evidently enough left to allow the formation of the hydrolysis product during drying. Further, some water is present in the atmosphere to react with ASA. Based on an ASA molecular weight of 322 grams per mole (see Appendix III) and a 1.5% ASA addition rate, only about 0.084% water needs to be present to completely hydrolyze the ASA. Taking into account that not all the ASA will be retained, that some ASA will volatilize from the sheet, and that some ASA is consumed as an ester with cellulose, the amount of water reacting with ASA to form the hydrolysis product is even less than 0.084%.

Conditioning Time

Continued esterification during conditioning, as shown in Fig. 25, is expected and is in keeping with the increases in sizing previously seen during conditioning. Hydrolysis during conditioning, as suggested by the results shown in Fig. 26 and 27, can be considered even more likely to occur during conditioning than esterification because of the greater atmospheric availability of water as noted previously and the decrease in cellulosic reactive sites due to previous esterification during drying. Thus, the results are reasonable.

Consumption of the ASA during conditioning, shown in Fig. 28, occurred and is to be expected from a functional group that is so reactive.[22] Further, if esterification and hydrolysis occur during conditioning, then ASA must be consumed.

The above ASA reaction results parallel the results Kamutzki and Krause[25] obtained with AKD very closely.

The decrease in the acid peak, occurring in the period of conditioning from one day to one week as shown in Fig. 26 was unexpected. The source of the loss may be restricted to two sources. First, the acid may be consumed in a secondary reaction, and second, the acid may be removed as the hydrolysis product through volatilization. The acid resulting from esterification would not be expected to be capable of removal through volatilization. Both of the above possibilities were investigated, and while it may be said there was some evidence for both possibilities, no firm conclusions could be drawn. A more detailed description of this investigation is presented in Appendix X.

ASA MIGRATION IN LAMINATED SHEETS

Size Tests

The size tests of laminated sheets shown in Fig. 29 and 30 yielded firm evidence of ASA migration during drying, and its ability to yield sizing after migrating. The source of the increase in sizing of Layer 3 during conditioning could be traced to two potential sources. One source is curing of the ASA already present in Layer 3. The second source was additional migration of ASA from Layer 1 to Layer 3 during conditioning. Migration during conditioning was ruled out as a source for the sizing level increase during conditioning. This resulted because Layer 3 of the sheet delaminated before conditioning displayed an increased sizing level with conditioning, as shown in Fig. 29. Since the sheet was removed from the ASA source during conditioning, no migration could have occurred. The increase in sizing during conditioning observed in Fig. 29 and 30 was instead due to curing of the ASA already present in Layer 3 from migration during drying.

The greater increase in sizing during conditioning shown in Fig. 30 in the samples dried 7 minutes as compared to those dried 20 minutes in Fig. 29 can be explained by observing that at the lower drying time the ASA does not have as great an opportunity to migrate and react to the ester as with a 20-minute drying time. Conditioning allows the migrated ASA to react to the cellulose ester. It should be noted that approximately similar size tests were obtained after one day of conditioning whether the samples were dried 7 minutes or 20 minutes.

The lack of sizing in Layer 3, observed when Layer 1 contained 0.15% ASA, can be explained by there being a lack of ASA available to volatilize. Clearly, some must be consumed in Layer 1 as the ester and the hydrolysis product, and this leaves less that can migrate to Layer 3.

Spectrometric Tests

The IR results observed in five layered sheets agree with the sizing results discussed above. Evidence for ASA migration was clearly observed in Layers 3, 4, and 5 in Fig. 32, 33, and 35, through both DRIFTS, and transmission IR spectrometry of sheet extracts.

Curing of the ASA to the ester was also clearly observed by DRIFTS in Fig. 32, 34, and 36.

In the five layered sheets, no evidence was observed of ASA migration during conditioning in Fig. 32, 34, and 35. Samples were compared in Fig. 35 by DRIFTS that remained laminated during conditioning and that were delaminated immediately after drying to prevent migration during conditioning. No conclusive differences in the ASA level were observed, and similar ASA consumption as the ester-acid product was seen in Fig. 36 and 37 for Layers 3 and 4, whether delamination occurred before conditioning or whether it did not. DRIFTS results from Layer 5 yielded data that were less reliable than those of Layers 3 and 4 due to the lower concentrations of species in Layer 5. The results for Layers 3 and 4 eliminated any firm possibility that ASA migration occurred during conditioning. This is not unexpected, since it has been previously noted that ASA is consumed rapidly during conditioning, thus eliminating it as a sizing source.

CONCLUSIONS

The data generated in this thesis indicate that ASA can form esters with cellulose in a papermaking system. Additionally, though the hydrolysis product is also readily formed in the system examined, it is unable to provide any sizing ability. Thus, the ester is the ASA reaction product that promotes sizing in this system.

Examination of the effects of drying variables on ASA sizing and reaction allows several conclusions to be made.

Increasing the drying temperature and drying time is beneficial to sizing development; however, overdrying of oven dried sheets is harmful to sizing.

Conditioning yields superior sizing, compared with unconditioned samples, in specimens where it may be expected some residual ASA remains. Little, if any, additional sizing is achieved when conditioning is extended from one day to one week.

An additional conclusion is that differences in drying technique (i.e., contact drying versus oven drying) may affect the sizing results. The reason for this difference cannot be provided by the data obtained in this thesis.

Increasing the drying temperature and drying time promotes the esterification reaction relative to the hydrolysis reaction, though hydrolysis does occur during drying.

Conditioning allows additional esterification and hydrolysis to occur, with hydrolysis occurring to a greater extent during conditioning, compared to during drying.

The third phase of this thesis allows several conclusions to be made. It is clear that ASA migrates as the unreacted ASA. More importantly, ASA that migrates can clearly yield sizing through esterification. The esterification may occur during and after drying. Additionally, ASA is rapidly consumed through reaction and does not migrate, in the system examined, during conditioning. That migration occurs during drying, but not during conditioning, is to be expected, since the vapor pressure of ASA would be lower at the conditioning temperature. The most important conclusion drawn from the third phase of this thesis is that migration and esterification of the ASA may be found in the same system. One phenomenon does not preclude the other.

SUGGESTIONS FOR FUTURE RESEARCH

The literature frequently discusses AKD research. ASA research is far less frequently published and any additional published ASA research would be useful.

The purpose of this thesis was largely to provide qualitative answers and to characterize the effects of process variables on the ASA sizing system. There is a clear opportunity for a more quantitative analysis of the ASA system than discussed in this thesis. The methods Lindstrom *et al.*,[35,37] and Dumas and Evans,[40] have used with AKD could easily be extended to an ASA system. Radioactively labelled ASA, in conjunction with sample combustion and careful extraction techniques could yield more information about ASA. The kinetics of the reaction and the influence of other papermaking chemical components could be examined.

A question raised during this thesis that could be examined is the effect of different types of drying on ASA sizing (i.e., contact drying *versus* oven drying). This area would have implications for laboratory testing of ASA. A sheet dried on a paper machine is actually dried in two ways - on the drum and off the drum. Drying a sheet completely in an oven, or on a drum, may not be the most realistic way to examine ASA sizing in the laboratory. An examination of this question could be approached using a carefully controlled pilot paper machine.

An additional question raised is whether the hydrolysis product vaporizes off the sheet to a significant extent. This could be answered using radioactive labelling of ASA as mentioned above.

ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. R. A. Stratton, the chairman of my thesis advisory committee. Thanks are also due to Dr. D. B. Easty and Dr. H. S. Dugal, who also served on my committee. These gentlemen provided many useful suggestions to me and were always supportive of my work.

I am also grateful to The Institute of Paper Chemistry and its member companies for providing the opportunity to perform the work presented here and for financially supporting it. The staff and students of the Institute should also be thanked for their friendship and kindness during my stay at the Institute.

LeRoy Borchardt performed the GC/MS work and deserves thanks for this. Special thanks go to Don Gilbert for allowing me to invade his laboratory so often and for providing assistance whenever I needed it. Additionally, I am grateful to Sally Berben for a great deal of help and technical advice provided while this thesis was in progress. This thesis would have been much more difficult without her assistance.

Finally, I would like to thank most of all my wife, Laura. Laura gave me love and support when I needed it, worked hard to support us financially, and was always willing to listen and understand me. Without Laura, this work could not have been accomplished by me.

LITERATURE CITED

1. Britt, K. W., ed. Handbook of Pulp and Paper Technology. Ch. 5-6, Van Nostrand Reinhold Company, New York, 1970. p. 380.

2. Mortimer, C. Chemistry, a conceptual approach. Third ed., D. Van Nostrand Company, New York, 1975.

3. Vinogradov, S.; Linnell, R. Hydrogen bonding. Van Nostrand Reinhold Company, New York, 1971.

4. Davison, R. W. 1986 TAPPI Papermakers Conference. p. 17-18.

5. Swanson, J. Internal sizing of paper and paperboard. TAPPI Monograph Series No. 33, 1971.

6. Davison, R. W., Tappi 58(3):48-57(March, 1975).

7. Strazdins, E., 1981 TAPPI Sizing Short Course Notes. p. 49.

8. Britt, K. W., ed.; Davison, R. W.; Spurlin, H. M. Handbook of Pulp and Paper Technology. Ch. 5-4, Van Nostrand Reinhold Company, New York, 1970. pp. 356-8.

9. Arnson, T. The adsorption of complex aluminum species by cellulosic fibers from dilute solutions of aluminum chloride and aluminum sulfate. Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wisconsin, June, 1980.

10. Dumas, D., 1981 TAPPI Sizing Short Course Notes. p. 63.

11. Johnson, R. G., Pulp Paper 60(13):66-7(Dec., 1986).

12. Maher, J. 1982 TAPPI new sizing methods and their effects on fiber, fillers and dyes - Seminar Notes. p. 37.

13. Brink, H.; Gaspar, L., 1983 TAPPI Sizing Seminar. p. 99.

14. Wurzburg, O. B.; Mazzarella, E. D., U.S. pat. 3,102,064(Aug. 27, 1963).

15. Williams, D.; Swanson, J. TAPPI CA Report No. 57. Sept. 1, 1975, p. 47.

16. Davis, J.; Roberson, W.; Weisgerber, C., Tappi 39(1):21(Jan., 1956).

17. Alberts, R., 1983 TAPPI Sizing Seminar. p. 111.

18. Weisgerber, C.; Hanford, C., Tappi 43(12):178A(Dec., 1960).

19. Miller, W. as referenced by Lund, R. Mobility and bonding of alkyl ketene dimer sizing. Master's Thesis, University of Washington, 1983.

20. Meyer, R., 1983 TAPPI Sizing Seminar. p. 93.

21. Wingrove, A.; Caret, R. Organic chemistry. Harper and Row, New York, 1981.

22. Fessenden, R.; Fessenden, J. Organic chemistry. Willard Grant Press, Boston, 1979.

23. Enke, M., Cellulose Chem. Technol. 7(4):487-500(July/Aug., 1973).

24. Pisa, L.; Murckova, E., Papir Celuloza 36(2):V15-18(Feb., 1981).

25. Kamutzki, W.; Krause, T., Papier 36(7):311-17(July, 1982).

26. Kamutzki, W.; Krause, T., Wochbl. Papierfabr. 111(7):215-16, 218-20, 222 (April 15, 1983).

27. Gupta, M., Tappi 63(3):29(March, 1980).

28. Rohringer, P.; Bernheim, M.; Werthemann, D., Tappi 68(1):83-6(Jan., 1985).

29. Metzler, R. Weyerhaeuser Technical Report No. 046-5201-07, Feb., 1983, as referenced by Lund, R. Mobility and bonding of alkyl ketene dimer sizing. Master's Thesis, University of Washington, 1983.

30. Merz, J.; Bernheim, M.; Rohringer, P., Papier 39(5):214-20(May, 1985).

31. Roberts, J.; Garner, D., Cellulose Chem. Technol. 18(3):275-82(May/ June 1984).

32. Roberts, J.; Garner, D., Tappi 68(4):118-21(April, 1985).

33. Poppel, E.; Bobu, E., Cellulose Chem. Technol. 19(6):719-728(Nov./Dec., 1985).

34. Nahm, S., J. Wood Chem. Technol. 6(1):89-112(March, 1986).

35. Lindstrom, T. XXI EUCEPA International Conference. Torremolinos, Spain, May 14-17, 1984, pp. 485-98.

36. Odberg, L.; Lindstrom, T. 1985 International Symposium on Wood and Pulping Chemistry - Technical Papers. Vancouver, British Columbia, Canada, August, 26-30, 1985, pp. 41-2.

37. Lindstrom, T.; Soderberg, G., Nordic Pulp Paper Res. J. 1(1):26-33, 42 (April, 1986).

38. Lindstrom, T., Nordic Pulp Paper Res. J. 1(1):34-42(April, 1986).

39. Lindstrom, T.; Soderberg, G., Nordic Pulp Paper Res. J. 1(2):39-45(June, 1986).

40. Dumas, D. H.; Evans, D. B. 1986 TAPPI Papermakers Conference. pp. 31-5.

41. Poppel, E.; Bobu, E., Cellulose Chem. Technol. 19(6):707-18(Nov./Dec., 1985).

42. Lindstrom, T.; Soderberg, G., Nordic Pulp Paper Res. J. 1(2):31-8(June, 1986).

43. Wasser, R. 1985 TAPPI Alkaline Papermaking Conference - Seminar Notes. pp. 17-20.

44. Cuculo, J., Textile Res. J. 41(4):321(April, 1971).

45. Cuculo, J., Textile Res. J. 41(5):375(May, 1971).

46. Johnson, E.; Cuculo, J., Textile Res. J. 43(5):283(May, 1973).

47. Allen, T.; Cuculo, J., ACS Symposium Series No. 10, 1975, p. 51.

48. Wadsworth, L.; Cuculo, J., ACS Symposium Series No. 49, 1977, p. 81.

49. Silverstein, R.; Bassler, G.; Morrill, T. Spectrometric identification of organic compounds. 4th ed., John Wiley and Sons, New York, 1981, pp. 95-137.

50. Suzuki, E. M.; Gresham, W. R., J. Forensic Sciences 31(3):931-6(July, 1986).

51. Ferraro, J. R.; Basile, L. J. Fourier transform infrared spectroscopy - techniques using fourier transform interferometry. Vol. III, Academic Press, New York, 1982, pp. 152-9.

52. Literature survey on cotton linters as a papermaking fiber. Project 1708-A, Progress Report One to Writing Paper Manufacturers Association, The Institute of Paper Chemistry, Appleton, Wisconsin, April 13, 1954, p. 45-7.

53. Eggert, A. The role of particle size and molecular weight on the adsorption and flocculation of polystyrene latex with poly(1,2-dimethyl-5-vinylpyridinium bromide). Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wisconsin, June, 1976.

54. T 205 om-81, TAPPI Standard Methods. 1981.

55. Hercules Sizing Tester Instruction Manual. Organics Dept. - Hercules, Inc., Wilmington, Delaware.

56. Maher, J. E., Pulp Paper 57(6):118-22(June, 1983).

57. Bowman, B. G.; Cuculo, J. A., ACS Symposium Series No. 58. 1977, p. 153-5.

58. Farley, C. E., 1985 TAPPI Alkaline Papermaking Conference. p. 77.

59. Strazdins, E., 1985 TAPPI Alkaline Papermaking Conference. p. 41.

60. Hill, C. G., Jr. An introduction to chemical engineering kinetics and reactor design. John Wiley and Sons, New York, 1977. p. 62.

61. Laboratory Procedure for Modified R-70 Emulsion. National Starch and Chemical Corp., Bridgewater, New Jersey.

62. Skoog, D. A.; West, D. M. Fundamentals of analytical chemistry. 3rd ed., Holt, Rinehart and Winston, New York, 1976. p. 42-88.

APPENDIX I

REACTION OF ASA WITH SYSTEM MATERIALS

The reaction of starch with ASA was observed as a peak at about 1737 cm^{-1} in a diffuse reflectance IR spectrum of a dried ASA emulsion (oven dried at 105°C for one hour) containing starch. Preparation of the emulsion is described in National Starch and Chemical Corporation literature.[61]

The reaction of ASA with the emulsifying agent was observed as a peak at about 1736 cm^{-1} in a transmission IR spectrum of an ASA-20% emulsifying agent mixture heated at 105°C for one hour in a convection oven.

No determinations of the precise natures of these reactions were made, since the very fact that the reactions produced peaks in the IR ester region meant the materials needed to be eliminated from the experimentation.

APPENDIX II

PREPARATION OF THE COTTON LINTERS PULP

The second cut cotton linters pulp used for this thesis was bleached with chlorine and hypochlorite, and extracted during the bleaching sequence by Alpha Cellulose Corporation. On obtaining the pulp, it was beaten in a laboratory Valley Beater at 2.5% consistency for 15 minutes to a Canadian Standard Freeness of 290 mL. Deionized water was used during this treatment. The pulp was then centrifuged, flaked, and air dried. Following this, 255 oven dry grams of pulp were Soxhlet extracted in 8 liters of 1:1 95% ethanol:chloroform for 48 hours. A 12-liter flask and a 2-liter extractor were used. The pulp was then exposed to the air for several hours to evaporate the solvents from the pulp, washed thoroughly in distilled water, air dried, and placed in polyethylene bags. Five batches of pulp were extracted in this manner.

APPENDIX III

GC/MS ANALYSIS OF THE ASA

GC/MS analysis utilized silated ASA hydrolysis product. The hydrolysis product was produced by intermittently mixing 7.5 grams of the ASA with 1.5 grams of distilled water by hand for two days. The material was then dried in a vacuum desiccator containing phosphorus pentoxide overnight. The material was then silated with Tri-Sil BSA. The temperature used in the GC/MS was 90-310°C, changing at the rate of 10°C per minute. The electron impact method at 70 electron volts was used in the mass spectrometer.

The GC elution curve of the silated ASA hydrolysis product isomers and a representative mass spectrum of one of the isomers are shown in Fig. 39 and 40.

It was determined that several ASA isomers existed, with most having a molecular weight of 322 grams per mole. This molecular weight was obtained using the peak at 484, seen in Fig. 40, as the molecular weight of the silated ASA hydrolysis product. The calculation is shown below.

Material	Weight
Silated ASA hydrolysis product	484
$2[-Si(CH_3)_2]$	- 146
2H	+ 2
Protonated ASA hydrolysis product	= 340
water	- 18
ASA	= 322

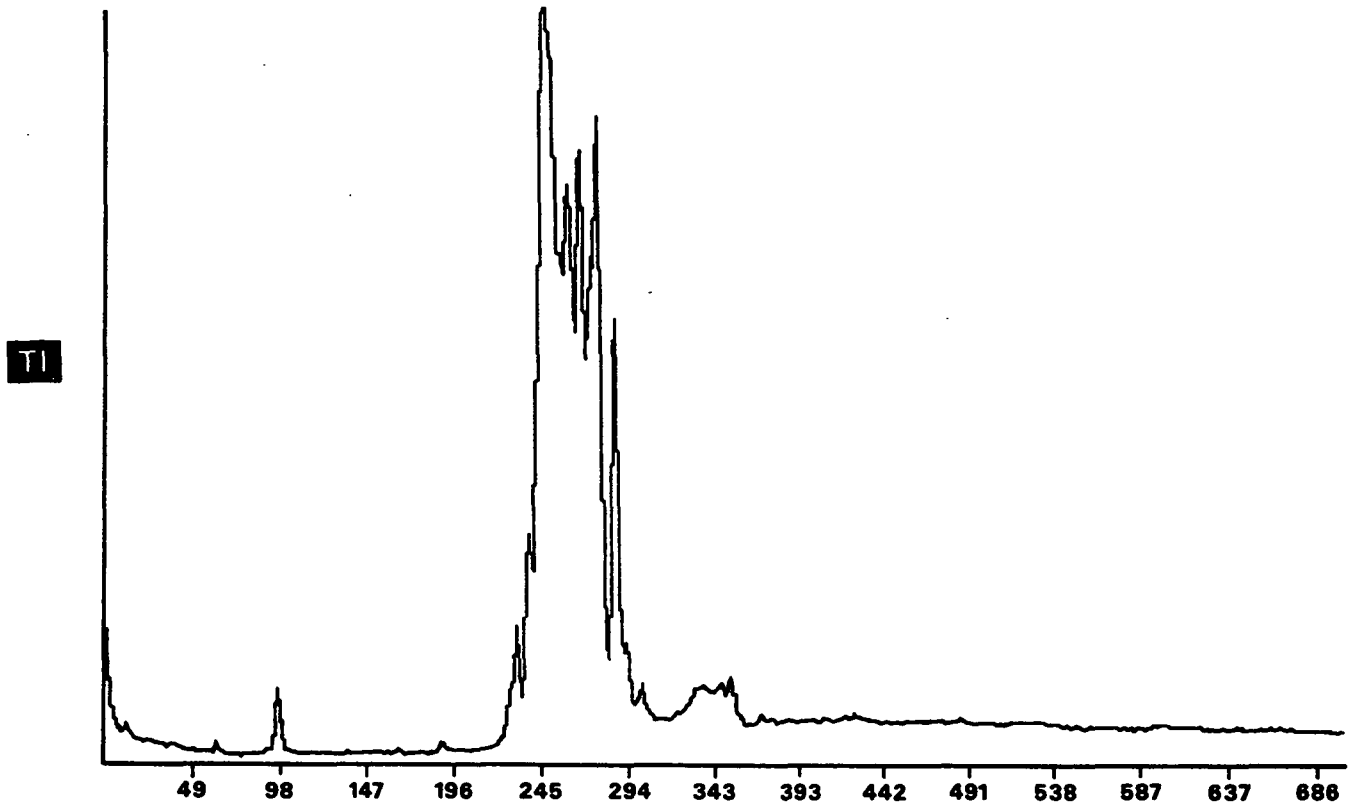


Figure 39. GC elution curve of the silated hydrolysis product.

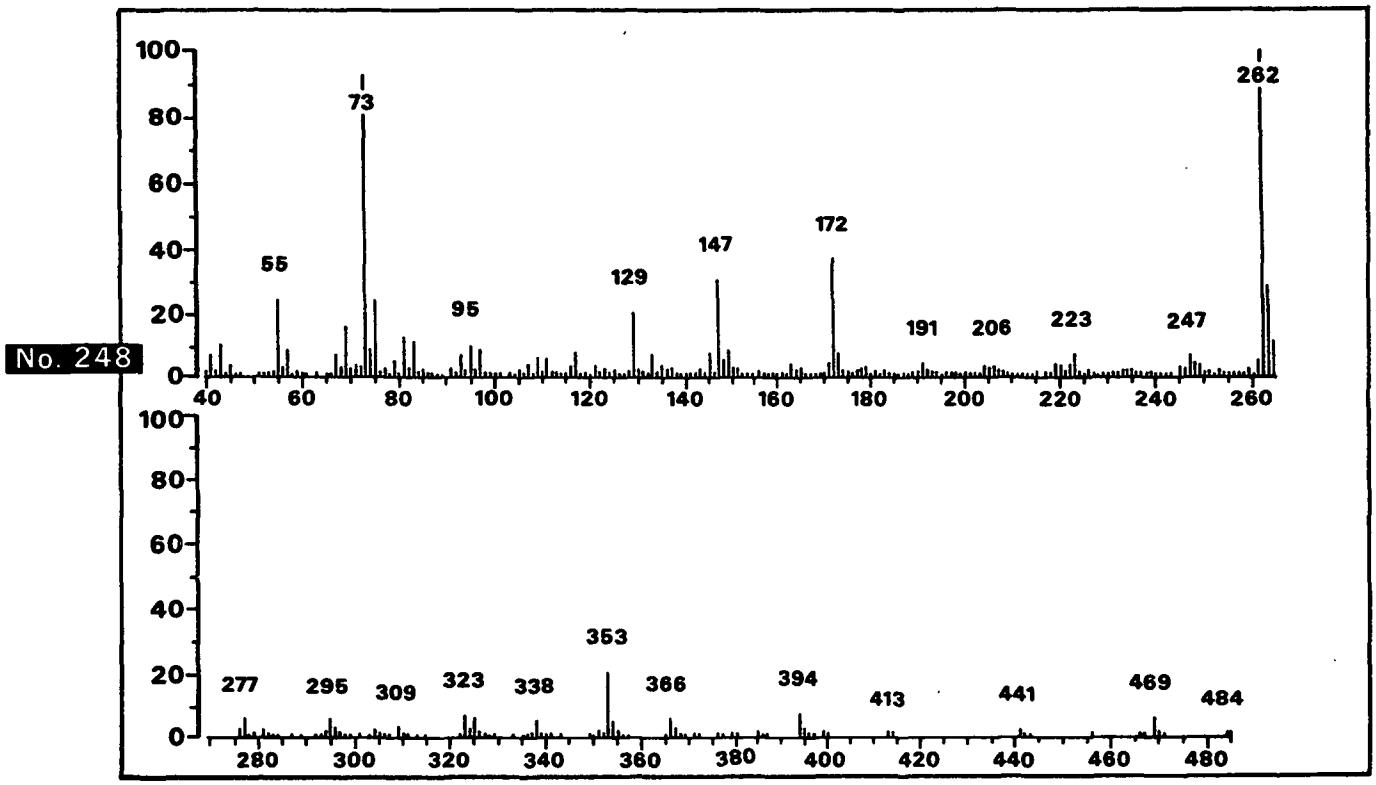


Figure 40. Mass spectrum of a representative silated ASA hydrolysis product isomer.

APPENDIX IV

PRODUCTION OF SHEETS CONTAINING THE ASA HYDROLYSIS PRODUCT

The tables included in this Appendix show the conditions under which sheets containing the hydrolysis product were produced. Also presented are the chemical additions made to each sheet. Actual amounts of the hydrolysis product retained were not measured, though DRIFTS spectra of some hydrolysis product sheets are shown in Fig. 41. The hydrolysis product may be clearly observed as a peak at about 1708 cm^{-1}. The Hercules Size Tests for the sheets described in this Appendix were all 0 seconds using 1% formic acid ink and a 65% reflectance endpoint, i.e., the sheets displayed no sizing.

Table 3. Chemical additions made to sheets produced at normal (0.026%) consistency.

Hydrolysis Product, %	Cationic Material	
	DMVPB, %	Alum, %
0.5[a]	0.15	0
1.0[a]	0.15	0
0.5[a]	0	0.35
0.5[a]	0	0.7
1.0[b]	0.15	0
0.5[b]	0.15	0
0.5[b]	0	0.7

[a]Cationic material added before the hydrolysis product.
[b]Cationic material added after the hydrolysis product.

Table 4. Chemical additions made to sheets produced at high consistencies.

Consistency, %	Hydrolysis Product, %	DMVPB, %	pH
2.06	42.7	0	7.5
1.24	0.978	0	7.5
1.24	4.89	0	7.5
1.24	9.78	0	7.5
1.24	19.56	0	7.5
1.24	39.12	0	7.5
1.07	1.92	0	7.5
1.07	9.6	0	7.5
1.07	19.1	0	7.5
1.07	1.92	0	4.0
1.07	9.6	0	4.0
1.07	19.1	0	4.0
1.0	0.984	0.15	7.5
1.0	2.46	0.15	7.5
1.0	4.91	0.15	7.5
1.0	7.37	0.15	7.5
1.0	9.84	0.15	7.5

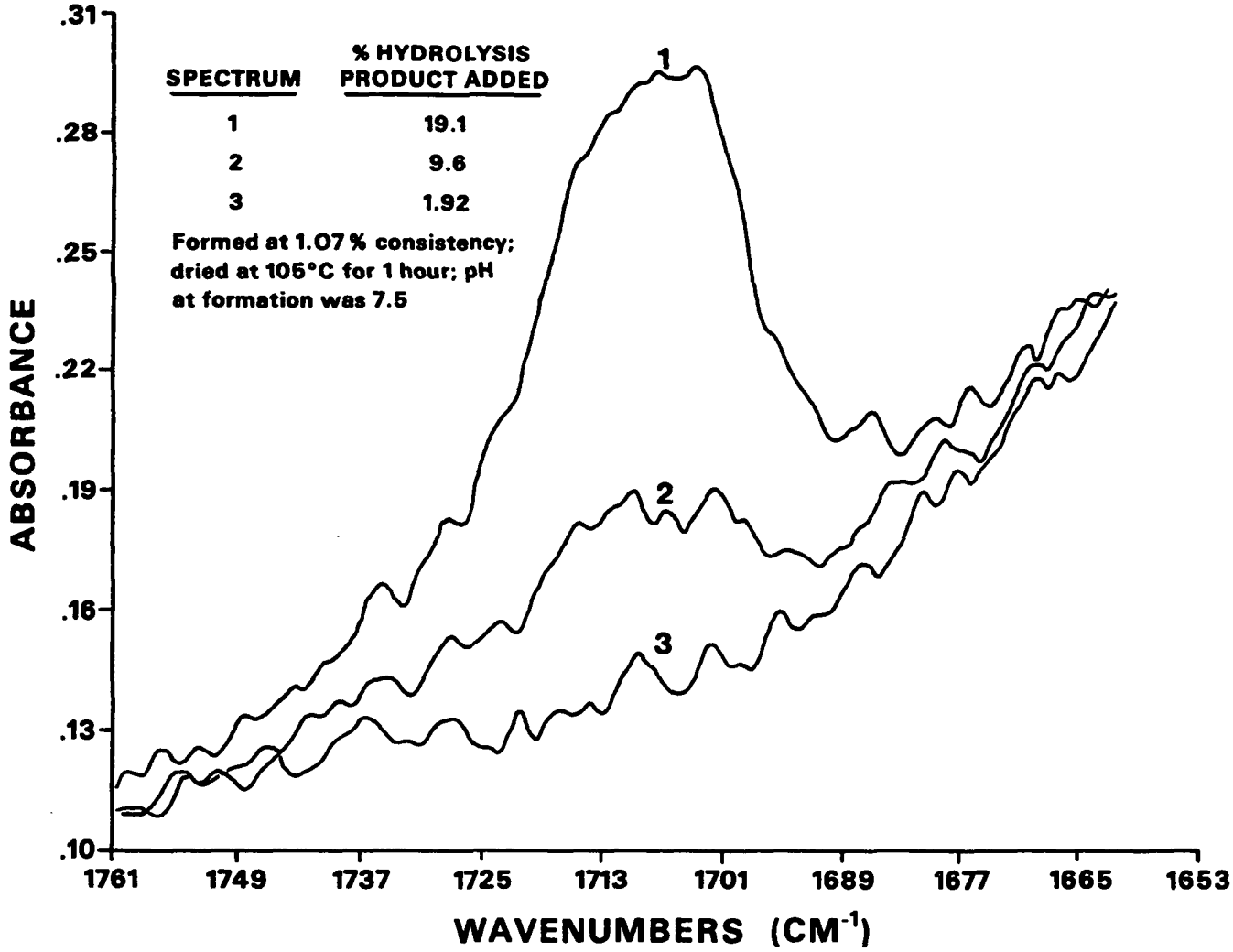


Figure 41. DRIFTS spectra of handsheets containing the ASA hydrolysis product that were formed at high consistency.

APPENDIX V

HERCULES SIZE TESTS OF SHEETS DRIED UNDER VARIED DRYING CONDITIONS

The data presented in the tables below are the Hercules Size Tests obtained in the second phase of this thesis using 10% formic acid ink and an 80% reflectance endpoint. All sheets contained 0.15% ASA and 0.15% DMVPB. The data in Tables 5-8 represent individual tests.

Table 5. Size tests from samples dried at 65°C.

Drying Time, minutes	Conditioning Time, days		
	0	1	7
10	0	4	1
20	1	8	2
40	1	41	8
60	2	47	16
90	6	139	27
120	10	116	25
150	31	111	14
180	29	99	9

Table 6. Size tests from samples dried at 75°C.

Drying Time, minutes	Conditioning Time, days 0	1	7
10	0	9	2
20	2	20	28
40	21	168	63
60	63	226	171
90	110	216	223
120	146	288	238
150	123	167	173
180	155	133	124

Table 7. Size tests from samples dried at 85°C.

Drying Time, minutes	Conditioning Time, days 0	1	7
10	2	46	18
20	20	112	88
40	126	427	304
60	207	426	448
90	372	385	338
120	410	445	291
150	420	201	253
180	365	225	89

Table 8. Size tests from samples dried at 105°C.

Drying Time, minutes	Conditioning Time, days 0	1	7
10	93	470	422
20	221	548	687
40	675	690	779
60	523	656	720
90	920	703	814
120	885	556	866
150	887	437	483
180	902	356	234

Table 9. Size tests from sheets contact dried (105°C surface temperature) and oven dried (105°C).

Drying Time, minutes	Type of Drying		Average Type of Drying	
	Oven	Contact	Oven	Contact
5	99/67	230/201	83	215
20	373/393	266/306	383	286
60	558/641	714/690	600	702
180	362/366	889/929	364	909

APPENDIX VI

PRECISION OF HERCULES SIZE TESTS

Using the data found in Table 9 in Appendix V, it is possible to calculate standard deviations for small sets of data with Eq. (2).[62]

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - x_a)^2}{N-1}} \qquad (2)$$

where: N = the number of measurements in a set (2)

x_i = individual size test

x_a = average of size tests

s = standard deviation

The results of these calculations are presented in Table 10.

Table 10. Standard deviations of Hercules Size Tests in Table 9.

Drying Time, minutes	Standard Deviation, seconds	
	Oven	Contact
5	23	21
20	14	28
60	59	17
180	3	28
Average:	25	24

The above results suggest a standard deviation from 20 to 30 seconds is a reasonable approximation for the Hercules Size Tests.

APPENDIX VII

SUBTRACTED INFRARED ABSORBANCE VALUES FROM ASA SHEETS AT PEAK POSITIONS

The tables below contain the values derived from subtracting a diffuse reflectance infrared spectrum of a sheet made only of cotton linters (oven dried for 90 minutes at 105°C; diffuse reflectance spectrum obtained immediately after drying) from the diffuse reflectance spectra of cotton linters sheets containing 1.5% ASA (the sheets also contained 0.15% DMVPB). All spectra were base line corrected from 400-4000 cm^{-1} before subtractions were performed over the range of 1350-2000 cm^{-1}. The resulting subtraction spectra were base line corrected from 1685-1900 cm^{-1} before measuring the peak heights in absorbance units at the approximate peak positions noted in cm^{-1} below.

Table 11. Absorbance values from a sample dried at 65°C that was unextracted and unconditioned.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0702	0.0722	0.0632	0.0574	0.0518	0.0498	0.0519	0.0460	0.0444
1785:	0.1867	0.2010	0.1784	0.1686	0.1504	0.1511	0.1547	0.1362	0.1313
1730:	0.0092	0.0075	0.0148	0.0151	0.0173	0.0237	0.0278	0.0302	0.0280
1710:	0.0029	0.0017	0.0104	0.0100	0.0129	0.0174	0.0238	0.0241	0.0216

Table 12. Absorbance values from a sample dried at 65°C that was conditioned one day and unextracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0181	0.0177	0.0138	0.0149	0.0156	0.0126	0.0136	0.0109	0.0104
1785:	0.0313	0.0252	0.0163	0.0203	0.0284	0.0166	0.0218	0.0095	0.0143
1730:	0.0771	0.0738	0.0812	0.0812	0.0706	0.0818	0.0765	0.0819	0.0779
1710:	0.1031	0.0900	0.0984	0.0975	0.0874	0.0916	0.0902	0.0816	0.0938

Table 13. Absorbance values from a sample dried at 65°C that was conditioned one week and unextracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0101	0.0100	0.0094	0.0082	0.0093	0.0082	0.0106	0.0103	0.0088
1785:	0.0078	0.0106	0.0100	0.0098	0.0126	0.0108	0.0095	0.0133	0.0073
1730:	0.0773	0.0727	0.0734	0.0747	0.0715	0.0708	0.0750	0.0679	0.0769
1710:	0.0704	0.0643	0.0610	0.0689	0.0646	0.0617	0.0694	0.0580	0.0793

Table 14. Absorbance values from a sample dried at 65°C that was unconditioned and then extracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0087	0.0079	0.0077	0.0088	0.0090	0.0072	0.0073	0.0081	0.0085
1785:	0.0045	0.0049	0.0070	0.0069	0.0094	0.0061	0.0063	0.0047	0.0066
1730:	0.0211	0.0181	0.0213	0.0268	0.0309	0.0323	0.0299	0.0265	0.0328
1710:	0.0096	0.0093	0.0112	0.0152	0.0159	0.0199	0.0174	0.0137	0.0196

Table 15. Absorbance values from a sample dried at 65°C that was conditioned one day and then extracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0068	0.0078	0.0082	0.0092	0.0063	0.0056	0.0066	0.0068	0.0060
1785:	0.0071	0.0064	0.0057	0.0047	0.0059	0.0087	0.0052	0.0077	0.0042
1730:	0.0396	0.0377	0.0392	0.0364	0.0331	0.0436	0.0370	0.0430	0.0360
1710:	0.0265	0.0227	0.0275	0.0230	0.0244	0.0305	0.0269	0.0300	0.0259

Table 16. Absorbance values from a sample dried at 65°C that was conditioned one week and then extracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0081	0.0052	0.0076	0.0082	0.0092	0.0062	0.0079	0.0093	0.0081
1785:	0.0099	0.0106	0.0116	0.0091	0.0077	0.0124	0.0085	0.0105	0.0088
1730:	0.0507	0.0475	0.0545	0.0453	0.0533	0.0540	0.0542	0.0524	0.0499
1710:	0.0385	0.0330	0.0371	0.0325	0.0376	0.0392	0.0368	0.0350	0.0337

Table 17. Absorbance values from a sample dried at 75°C that was unextracted and unconditioned.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0618	0.0569	0.0515	0.0518	0.0501	0.0413	0.0454	0.0416	0.0444
1785:	0.1821	0.1606	0.1456	0.1491	0.1471	0.1256	0.1285	0.1276	0.1343
1730:	0.0035	0.0047	0.0103	0.0227	0.0240	0.0275	0.0288	0.0415	0.0396
1710:	0.0014	0.0019	0.0059	0.0119	0.0178	0.0178	0.0179	0.0297	0.0325

Table 18. Absorbance values from a sample dried at 75°C that was conditioned one day and unextracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0214	0.0212	0.0265	0.0304	0.0208	0.0193	0.0181	0.0135	0.0199
1785:	0.0423	0.0364	0.0690	0.0867	0.0521	0.0411	0.0382	0.0257	0.0491
1730:	0.0621	0.0648	0.0505	0.0566	0.0742	0.0658	0.0684	0.0817	0.0718
1710:	0.0771	0.0777	0.0603	0.0671	0.0902	0.0766	0.0790	0.0827	0.0858

Table 19. Absorbance values from a sample dried at 75°C that was conditioned one week and unextracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0107	0.0107	0.0094	0.0101	0.0097	0.0070	0.0100	0.0072	0.0101
1785:	0.0103	0.0108	0.0122	0.0112	0.0137	0.0119	0.0115	0.0114	0.0115
1730:	0.0875	0.0838	0.0796	0.0835	0.0857	0.0715	0.0868	0.0822	0.0764
1710:	0.1001	0.0891	0.0717	0.0832	0.0767	0.0656	0.0783	0.0768	0.0750

Table 20. Absorbance values from a sample dried at 75°C that was unconditioned and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0065	0.0091	0.0086	0.0076	0.0069	0.0062	0.0066	0.0078	0.0083
1785:	0.0075	0.0087	0.0099	0.0099	0.0066	0.0122	0.0078	0.0130	0.0090
1730:	0.0181	0.0256	0.0379	0.0330	0.0280	0.0441	0.0386	0.0511	0.0360
1710:	0.0120	0.0116	0.0185	0.0199	0.0184	0.0262	0.0219	0.0286	0.0199

Table 21. Absorbance values from a sample dried at 75°C that was conditioned one day and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0087	0.0086	0.0089	0.0082	0.0068	0.0090	0.0087	0.0078	0.0084
1785:	0.0056	0.0075	0.0068	0.0099	0.0102	0.0095	0.0067	0.0122	0.0099
1730:	0.0368	0.0449	0.0398	0.0456	0.0611	0.0691	0.0382	0.0631	0.0458
1710:	0.0238	0.0235	0.0245	0.0279	0.0353	0.0458	0.0219	0.0375	0.0293

Table 22. Absorbance values from a sample dried at 75°C that was conditioned one week and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0074	0.0107	0.0075	0.0085	0.0064	0.0084	0.0080	0.0096	0.0081
1785:	0.0128	0.0103	0.0127	0.0114	0.0115	0.0111	0.0127	0.0098	0.0079
1730:	0.0605	0.0622	0.0668	0.0687	0.0606	0.0552	0.0545	0.0636	0.0522
1710:	0.0395	0.0413	0.0429	0.0401	0.0372	0.0370	0.0371	0.0387	0.0330

Table 23. Absorbance values from a sample dried at 85°C that was unextracted and unconditioned.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0578	0.0492	0.0424	0.0427	0.0312	0.0286	0.0287	0.0247	0.0193
1785:	0.1614	0.1459	0.1182	0.1172	0.0898	0.0738	0.0812	0.0645	0.0466
1730:	0.0116	0.0159	0.0215	0.0323	0.0318	0.0309	0.0450	0.0390	0.0437
1710:	0.0091	0.0109	0.0160	0.0236	0.0256	0.0269	0.0381	0.0338	0.0383

Table 24. Absorbance values from a sample dried at 85°C that was conditioned one day and unextracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0168	0.0157	0.0162	0.0123	0.0100	0.0094	0.0103	0.0090	0.0085
1785:	0.0342	0.0341	0.0341	0.0173	0.0168	0.0125	0.0111	0.0086	0.0081
1730:	0.0716	0.0681	0.0621	0.0737	0.0613	0.0622	0.0675	0.0607	0.0627
1710:	0.0856	0.0824	0.0745	0.0722	0.0647	0.0628	0.0644	0.0562	0.0600

Table 25. Absorbance values from a sample dried at 85°C that was conditioned one week and unextracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0113	0.0087	0.0085	0.0082	0.0081	0.0070	0.0084	0.0066	0.0056
1785:	0.0066	0.0085	0.0087	0.0070	0.0096	0.0073	0.0077	0.0087	0.0098
1730:	0.0823	0.0711	0.0683	0.0655	0.0620	0.0580	0.0615	0.0523	0.0553
1710:	0.0908	0.0637	0.0591	0.0552	0.0518	0.0485	0.0484	0.0389	0.0464

Table 26. Absorbance values from a sample dried at 85°C that was unconditioned and then extracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0063	0.0055	0.0059	0.0076	0.0073	0.0068	0.0074	0.0070	0.0074
1785:	0.0100	0.0076	0.0074	0.0095	0.0091	0.0105	0.0072	0.0083	0.0113
1730:	0.0355	0.0369	0.0399	0.0400	0.0437	0.0514	0.0470	0.0429	0.0496
1710:	0.0218	0.0220	0.0249	0.0235	0.0251	0.0306	0.0274	0.0255	0.0294

Table 27. Absorbance values from a sample dried at 85°C that was conditioned one day and then extracted.

	Minutes Of Drying								
cm^{-1}	10	20	40	60	90	120	150	180	210
1865:	0.0093	0.0071	0.0090	0.0072	0.0101	0.0078	0.0085	0.0060	0.0074
1785:	0.0070	0.0056	0.0055	0.0064	0.0070	0.0063	0.0057	0.0072	0.0079
1730:	0.0388	0.0359	0.0391	0.0373	0.0561	0.0406	0.0404	0.0450	0.0455
1710:	0.0222	0.0234	0.0225	0.0257	0.0368	0.0257	0.0263	0.0319	0.0299

Table 28. Absorbance values from a sample dried at 85°C that was conditioned one week and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0074	0.0085	0.0065	0.0079	0.0080	0.0082	0.0082	0.0090	0.0083
1785:	0.0072	0.0086	0.0087	0.0086	0.0074	0.0083	0.0109	0.0084	0.0077
1730:	0.0467	0.0513	0.0479	0.0478	0.0454	0.0404	0.0528	0.0485	0.0454
1710:	0.0333	0.0346	0.0334	0.0316	0.0298	0.0278	0.0377	0.0327	0.0290

Table 29. Absorbance values from a sample dried at 105°C that was unextracted and unconditioned.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0463	0.0416	0.0284	0.0225	0.0170	0.0097	0.0114	0.0081	0.0077
1785:	0.1416	0.1312	0.0935	0.0747	0.0492	0.0250	0.0251	0.0171	0.0175
1730:	0.0157	0.0245	0.0335	0.0446	0.0457	0.0391	0.0513	0.0408	0.0453
1710:	0.0133	0.0164	0.0243	0.0330	0.0358	0.0304	0.0394	0.0348	0.0329

Table 30. Absorbance values from a sample dried at 105°C that was conditioned one day and unextracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0192	0.0108	0.0082	0.0084	0.0105	0.0067	0.0063	0.0067	0.0070
1785:	0.0350	0.0177	0.0098	0.0090	0.0060	0.0056	0.0053	0.0069	0.0059
1730:	0.0526	0.0679	0.0633	0.0546	0.0451	0.0457	0.0478	0.0425	0.0415
1710:	0.0617	0.0815	0.0543	0.0566	0.0367	0.0332	0.0327	0.0334	0.0346

Table 31. Absorbance values from a sample dried at 105°C that was conditioned one week and unextracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0075	0.0068	0.0062	0.0062	0.0078	0.0064	0.0055	0.0062	0.0064
1785:	0.0044	0.0062	0.0093	0.0055	0.0086	0.0090	0.0098	0.0083	0.0100
1730:	0.0608	0.0588	0.0539	0.0468	0.0413	0.0474	0.0430	0.0406	0.0393
1710:	0.0553	0.0493	0.0407	0.0393	0.0301	0.0290	0.0276	0.0268	0.0235

Table 32. Absorbance values from a sample dried at 105°C that was unconditioned and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0064	0.0081	0.0077	0.0072	0.0093	0.0071	0.0069	0.0097	0.0065
1785:	0.0053	0.0065	0.0060	0.0068	0.0057	0.0038	0.0064	0.0075	0.0072
1730:	0.0177	0.0210	0.0295	0.0258	0.0289	0.0328	0.0333	0.0424	0.0331
1710:	0.0098	0.0093	0.0155	0.0125	0.0145	0.0164	0.0174	0.0207	0.0179

Table 33. Absorbance values from a sample dried at 105°C that was conditioned one day and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0048	0.0051	0.0071	0.0047	0.0069	0.0086	0.0059	0.0057	0.0081
1785:	0.0068	0.0043	0.0031	0.0043	0.0072	0.0063	0.0075	0.0059	0.0036
1730:	0.0376	0.0263	0.0265	0.0235	0.0447	0.0328	0.0360	0.0382	0.0310
1710:	0.0260	0.0152	0.0149	0.0163	0.0270	0.0172	0.0213	0.0231	0.0168

Table 34. Absorbance values from a sample dried at 105°C that was conditioned one week and then extracted.

	Minutes Of Drying								
	10	20	40	60	90	120	150	180	210
cm^{-1}									
1865:	0.0082	0.0095	0.0095	0.0067	0.0092	0.0085	0.0089	0.0101	0.0086
1785:	0.0076	0.0095	0.0124	0.0101	0.0084	0.0108	0.0104	0.0108	0.0117
1730:	0.0317	0.0362	0.0332	0.0352	0.0334	0.0369	0.0437	0.0378	0.0394
1710:	0.0169	0.0212	0.0172	0.0216	0.0164	0.0192	0.0236	0.0218	0.0211

Table 35. Absorbance values from a sample dried at 85°C that was unextracted and unconditioned. These data were used only to produce Fig. 21.

	Minutes of Drying								
	10	20	40	60	90	120	150	180[a]	210
cm^{-1}									
1865:	0.0556	0.0504	0.0429	0.0410	0.0372	0.0296	0.0241		0.0244
1785:	0.1567	0.1515	0.1252	0.1159	0.1107	0.0881	0.0717		0.0645
1730:	0.0092	0.0133	0.0174	0.0216	0.0344	0.0429	0.0352		0.0410
1710:	0.0058	0.0091	0.0138	0.0175	0.0286	0.0351	0.0301		0.0343

[a]Data from 180 minutes of drying time were not collected because the sample was destroyed.

APPENDIX VIII

SIZING DATA FROM LAMINATED SHEETS

The data presented in Table 36 are the Hercules Size Tests obtained in the third phase of this thesis. Ink containing no formic acid, and an 85% reflectance end point, were used.

Table 36. Size tests from laminated sheets.

Drying Time, minutes	Conditioning Time, days			
	0	1	4	7
7[a]	6/3	975/1133	947/1111	913/1040
20[a]	921/1150	973/1253	991/1232	936/1227
20[b]	1473	1710	1582	--

[a]Samples remained laminated during conditioning.
[b]Samples were delaminated before conditioning.

APPENDIX IX

INFRARED DATA FROM CONTACT DRIED SHEETS

The data in Table 37 were collected from a sheet (one layered) containing 1.5% ASA and 0.15% DMVPB. The sheet was contact dried.

The IR data in Table 38 were collected from Layers 3-5 of laminated sheets contact dried 20 minutes.

Table 37. Subtractive DRIFTS absorbance results at approximate peak positions.

	Minutes of Drying							
cm^{-1}	0.5	1	3	5	7.5	10	15	25
1865:	0.0625	0.0490	0.0418	0.0492	0.0391	0.0407	0.0357	0.0295
1785:	0.1691	0.1443	0.1221	0.1513	0.1194	0.1228	0.1075	0.0933
1730:	0.0100	0.0136	0.0182	0.0241	0.0265	0.0310	0.0289	0.0313
1710:	0.0064	0.0100	0.0144	0.0201	0.0225	0.0268	0.0262	0.0285

Table 38. Subtractive DRIFTS absorbance results at approximate peak positions from Layers 3-5 of laminated sheets.

		Conditioning Time, days			
cm^{-1}	Layer	0	1	7	7[a]
1865:	3	0.0086	0.0071	0.0060	0.0076
1865:	4	0.0084	0.0083	0.0066	0.0066
1865:	5	0.0068	0.0095	0.0068	0.0069
1785:	3	0.0060	0.0031	0.0031	0.0036
1785:	4	0.0074	0.0042	0.0048	0.0036
1785:	5	0.0043	0.0049	0.0037	0.0020
1730:	3	0.0084	0.0102	0.0147	0.0117
1730:	4	0.0064	0.0085	0.0109	0.0122
1730:	5	0.0034	0.0043	0.0052	0.0005
1710:	3	0.0058	0.0082	0.0129	0.0100
1710:	4	0.0055	0.0050	0.0109	0.0102
1710:	5	0.0026	0.0019	0.0044	-0.0008

[a]Delaminated before conditioning one week and then testing.

APPENDIX X

DESCRIPTION OF THE INVESTIGATION OF THE DECREASE IN THE ACID PEAK DURING CONDITIONING

The decrease in the acid after one week of conditioning, from the level observed after one day of conditioning, as shown in Fig. 26, could be attributed to a reaction of the acid, and/or volatilization of the ASA hydrolysis product.

An IR peak at approximately 1580 cm^{-1} appeared to intermittently develop in sheets as the acid level decreased. This could be considered indirect evidence of a reaction of the acid. The peak proved to be unextractable in toluene or 1,2-dichloroethane, and no data could be gathered to verify the peak's source.

In some cases sheets to which the hydrolysis product was added displayed decreases, during conditioning, in the IR peak resulting from the hydrolysis product at 1710 cm^{-1}. No evidence of the formation of a peak at 1580 cm^{-1} was observed. These decreases were small and not always apparent, but could be considered evidence for hydrolysis product volatilization.

As an investigation of the disappearance of the acid group during conditioning was not within the boundaries of investigation of this thesis, no further attempts were made to determine the source of the acid's disappearance.